Ferromagnetism and Charge Order from a Frozen Electron Configuration in Strained Epitaxial LaCoO$_3$

G. E. Sterbinsky,[1,*] R. Nanguneri,[2] J. X. Ma,[3] J. Shi,[3] E. Karapetrova,[1] J. C. Woicik,[4]
H. Park,[2,5] J.-W. Kim,[1] and P. J. Ryan[1,6]
[1]*Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA*
[2]*Department of Physics, University of Illinois at Chicago, Chicago, Illinois 60607, USA*
[3]*Department of Physics and Astronomy, University of California, Riverside, California 92521, USA*
[4]*National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*
[5]*Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA*
[6]*School of Physical Sciences, Dublin City University, Dublin 9, Ireland*

(Received 17 January 2017; revised manuscript received 8 March 2018; published 8 May 2018)

We report ordering of the cobalt electron configuration in ferromagnetic strained epitaxial LaCoO$_3$. Specifically, the presence of charge order is demonstrated from distinct features of the resonant cobalt contribution to superstructure reflections. Density functional theory calculations show that the observed order is consistent with the spin-state periodicity predicted to give rise to ferromagnetism in LaCoO$_3$. Through the modification of symmetry by strain, concurrent frozen charge and spin-state order are stabilized, giving rise to long-range magnetic order.

DOI: 10.1103/PhysRevLett.120.197201

Correlated electron physics is heavily dependent upon the interplay between physical parameters such as spin, charge, and lattice. Because of coupling between these parameters, subtle changes in one can lead to significant and unexpected changes in another [1,2]. For instance, lattice distortions can dramatically alter the properties of materials with correlated electrons, such as La$_{1-x}$Sr$_x$MnO$_3$, which can be driven from metal to insulator and ferromagnet to antiferromagnet via epitaxial strain [3]. Subtle lattice distortions can also give rise to ferromagnetism in a paramagnet, as found in LaCoO$_3$, which becomes ferromagnetic under tensile strain [4,5]. While recent studies have demonstrated that a strain-induced increase in the average Co─O bond length, i.e., an increase in the oxygen octahedral volume, is critical to the appearance of ferromagnetism [6,7], the exact nature of the microscopic mechanism by which the lattice couples to spin is unclear, and several models of the atomic characteristics and magnetic exchange that give rise to ferromagnetism in LaCoO$_3$ have been proposed [8–14].

Bulk LaCoO$_3$ is rhombohedral with pseudocubic-lattice parameters of 3.830 Å and 90.7° [Fig. 1(a)] [15–17]; it is a nonmagnetic insulator below 110 K, a paramagnetic semiconductor between 110 and 500 K, and a paramagnetic metal above 500 K. In the nonmagnetic phase, all Co^{3+} ions are in the low spin (LS) $t_{2g}^6 e_g^0$ state, and higher-temperature phase transitions result from changes in the Co^{3+} spin state to intermediate spin (IS) $t_{2g}^5 e_g^1$ and/or high spin (HS) $t_{2g}^4 e_g^2$ configurations [Fig. 1(b)] [18]. Though the details of the spin states present in the paramagnetic phases of LaCoO$_3$ are debated, one possible model supported by experiment [18,19] and theory [20–23] implicates a mixture of LS and HS Co^{3+} as responsible for the paramagnetic semiconducting phase up to 350 K. In this model, thermally-driven cooperative oxygen displacements cause the formation of two Co sites ordered in a rocksalt-type arrangement. In one site, Hund exchange stabilizes cobalt in the HS state, and in the other, cobalt remains in the LS configuration. The order is both short range and dynamic, thus giving rise to paramagnetism [19].

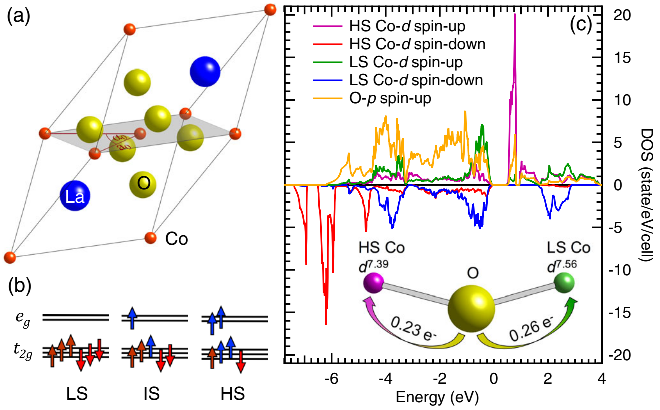

FIG. 1. (a) A schematic of the rhombohedral bulk LaCoO$_3$ unit cell showing a_0 and α_0. (b) Schematic energy-level diagrams of Co^{3+} LS, IS, and HS configurations. (c) The calculated DOS of strained ferromagnetic LaCoO$_3$. (Inset) A schematic of the Co─O─Co bond showing the charge transfer from oxygen to HS and LS cobalt.

While recent studies have explored the origin of ferromagnetism in $LaCoO_3$ thin films, multiple competing models have been proposed, including ferromagnetism resulting from defects [8,9], orbital order [10], or spin-state order [11–14]. This latter model is supported by both experiment and computational calculations, yet the specific spin-state order present has not been resolved. Experiments have shown the presence of vertical lattice modulations that appear correlated with spin-state order [13,14]. However, lattice stripes are not universally observed in ferromagnetic $LaCoO_3$ films [7,24,25]; therefore they cannot generally account for the ferromagnetism therein. On the other hand, density functional theory calculations indicate that the ground state of strained $LaCoO_3$ is ferromagnetic, with the same rocksalt-type arrangement of HS and LS Co^{3+} ions hypothesized to exist in bulk $LaCoO_3$ [11,12].

Here, we reveal details of $LaCoO_3$'s atomic and electronic structure that bring key features of the microscopic mechanism responsible for the stabilization of ferromagnetism to light. Specifically, the presence of charge order in a $LaCoO_3$ film grown on $SrTiO_3$, which imposes 2.0% tensile strain and gives rise to ferromagnetism below 80 K [26,27], is demonstrated from distinct features of the Co K-edge resonant x-ray scattering at particular superstructure reflections. Density functional theory plus U ($\mathrm{DFT}+U$) calculations show this order is characteristic of the spin-state periodicity predicted to bring about ferromagnetism in $LaCoO_3$. Charge and spin-state order arise through the stabilization of an oxygen octahedral breathing distortion, thereby precipitating the emergence of ferromagnetic order. These results indicate that the tendency for ordering of the local structure under stress, or other distortive forces, can be a significant factor in driving spin-state and thereby magnetic-phase transitions.

In order to probe the details of the electronic structure of $LaCoO_3$ in which cobalt electron-configuration order is present, we have applied $\mathrm{DFT}+U$ for both 20-atom and 40-atom supercells of tetragonal symmetry using the projector augmented wave method as implemented in the Vienna *ab initio* simulation package [28–30]. Our choice of the Hubbard interaction parameters are $U = 4.5$ eV and $J = 1.0$ eV [31]. For each unit cell, we fixed the lattice length along the a and b axes to the experimentally determined value of 3.905 Å, which is equal to the lattice constant of $SrTiO_3$. The cell dimension along the c axis and internal atomic positions of all atoms were relaxed. Spin-state order of 1 : 1 HS and LS was imposed on the cobalt atoms. The HS site has a magnetic moment of $\sim 3\ \mu_B$, which corresponds to three unpaired d electrons while the LS site has a negligible moment. After structural relaxation, the HS sites have a larger octahedral volume of $0.0107\ \mathrm{nm}^3$ compared to $0.0098\ \mathrm{nm}^3$ for the LS sites, thus establishing an octahedral breathing distortion. To confirm the stability of ferromagnetism in this arrangement, ferromagnetic order of the HS cobalt ions was imposed on the twenty-atom unit cell and antiferromagnetic order with wave vector (π, π, π) on the forty-atom unit cell. The ferromagnetic configuration is 14.25 meV/Co lower in energy than the antiferromagnetic configuration. The calculated density of states (DOS) of the ferromagnetic $LaCoO_3$ film is shown in Fig. 1(c).

In concert with the spin-state ordering, charge disproportionation occurs between the cobalt HS and LS sites. The cobalt d-orbital charge difference, calculated by Bader's Method [32], is 0.17 electrons. This originates from the covalent nature of the Co─O bonds such that the d^6 configuration is closer to d^7 with more charge transferred from oxygen to LS cobalt due to the reduced octahedral volume as illustrated in the inset to Fig. 1(c). Thus, charge and spin-state order are interdependent.

The structure of epitaxial $LaCoO_3$ is revealed by x-ray scattering, carried out at beamlines 6-ID-B and 33-BM-C of the Advanced Photon Source at room temperature. Incident x-ray energy was selected by a Si (111) double-crystal monochromator, and the scattered intensity was collected with a solid-state point detector. Approximately 20 nm thick $LaCoO_3$ films were deposited on $SrTiO_3$ (001) and $LaAlO_3$ (001) single-crystal substrates by pulsed-laser deposition in 1 mTorr of oxygen at 1023 K, capped with two unit cells of $SrTiO_3$, and annealed in 760 Torr of oxygen for two hours at 853 K. Previous studies have revealed the $LaCoO_3$ film on $SrTiO_3$ is ferromagnetic below ~80 K, while the $LaCoO_3$ film on $LaAlO_3$ shows paramagnetic or spin glass like behavior at low temperatures. Both films are insulating [26,27]. In $LaCoO_3$ on $SrTiO_3$, the oxygen octahedra are distorted relative to bulk $LaCoO_3$, having an increased average Co─O bond length and an average difference of 0.043 Å between in-plane and out-of-plane Co─O bond lengths, whereas a negligible difference between in-plane and out-of-plane Co─O bond lengths is found in $LaCoO_3$ on $LaAlO_3$ [6].

The reciprocal space map (RSM) of the $L = 2.0455$ reciprocal-lattice unit (RLU) plane [Fig. 2(a)] indicates that the $LaCoO_3$ film on $SrTiO_3$ is epitaxially coherent, i.e., lattice matched to the substrate [33]. Further distortion of the film is revealed by L scans taken through multiple $(0k3)$ and $(h\bar{2}3)$ reflections, [Figs. 2(b), 2(c)]. With constant h, the position of the film peak shifts to larger L as k increases. Conversely, the film peak position does not change for constant k. Schematic reciprocal-space lattices of the film and substrate discerned from the diffraction measurements are shown in Fig. 2(d). Transformation to real space reveals that the net effect is a shear distortion as illustrated in Fig. 2(e). From further refinement, the pseudocubic-lattice parameters are found to be $a = 3.905 \pm 0.003$ Å, $b = 3.903 \pm 0.004$ Å, $c = 3.781 \pm 0.018$ Å, $\alpha = 90.46° \pm 0.42°$, $\beta = 89.95° \pm 0.81°$, and $\gamma = 89.95° \pm 0.95°$ [16]. Having pseudocubic-lattice parameters where $a = b \neq c$, and at least one angle not equal to 90°, indicates

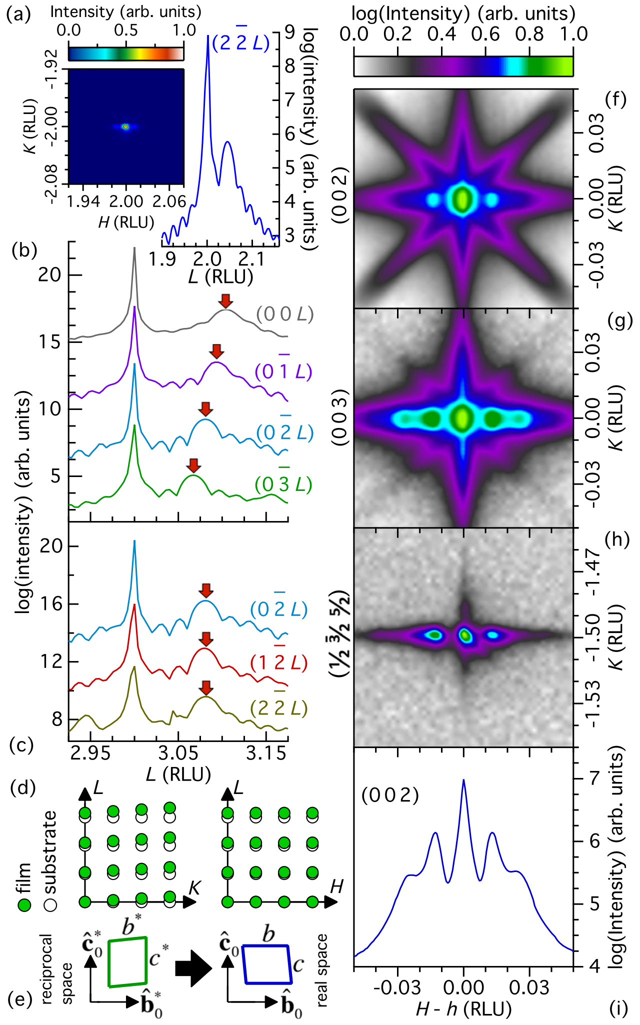

FIG. 2. (a) An L scan through the $(2\bar{2}2)$ reflection of $LaCoO_3$ on $SrTiO_3$. Inset: RSMs measured in the $L = 2.0455$ RLU plane [33]. The film peak is located at $H = 2$ RLU and $K = -2$ RLU, indicating that the film is lattice matched to the substrate. L scans through reflections with (b) $h = 0$ and (c) $k = -2$. (d) Schematic reciprocal lattices of the film and substrate. (e) Schematic film reciprocal-space and real-space unit cells (dimensions are exaggerated for clarity). RSMs in $L = l$ planes intersecting the (f) (002), (g) (003), and (h) $(\frac{1}{2}\frac{\bar{3}}{2}\frac{5}{2})$ film reflections. (i) An H scan through the film (002) reflection.

a reduction in the symmetry from rhombohedral in bulk to monoclinic [34,35]. In this symmetry, the coexistence of two unique cobalt sites is possible. Additionally, a $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ film reflection is present (not shown). The $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ reflection is bulk structure-factor forbidden, and here, it likely results from alternation of the oxygen octahedral volume between the two Co sites.

In addition to the reduction in symmetry, a lattice modulation develops in the pseudocubic [100] direction. This is evident from the satellite peaks with unvarying in-plane momentum transfer flanking the (002) and (003) film reflections [Figs. 2(f), 2(g), and 2(i)]. From the distance between satellites, the period of the modulation is determined to be ~28 nm. Scattering at the $(00l)$ reflections is only sensitive to changes in the vertical separation between atoms, i.e., in the direction of the substrate c axis $(\hat{\mathbf{c}}_0)$. Thus, transverse atomic displacements give rise to the lattice modulation. This is consistent with other reports of lattice modulations in oxide thin films [36,37]. Additionally, the half-order superstructure $(\frac{1}{2}\frac{\bar{3}}{2}\frac{5}{2})$ film reflection exhibits satellites with in-plane momentum transfer identical to those of the $(00l)$ film reflections [Fig. 2(h)]. In perovskites, half-order reflections typically result from doubling of the cubic unit cell that occurs when oxygen octahedral rotations are present [7,38]. Thus, the observed satellites demonstrate that the oxygen ions are modulated in concert with the metal ions in the film. The modulation forms along the pseudocubic a axis, which is perpendicular to the b and c axes. On the other hand, the pseudocubic angle between the b and c axes deviates from 90°, as in the bulk rhombohedral structure, indicating the lattice compensates for changes in the pseudocubic angle by forming a uniaxial lattice modulation. Subsequently, the film is stabilized with a single structural domain type where the tilt of the pseudocubic c axis is always in the same direction.

The presence of a single structural domain type preserves the uniqueness of the crystallographic directions within the film. Thus, specific half-order reflections will be sensitive to unique sets of crystallographic planes within the monoclinic structure, and charge order can be observed by employing resonant x-ray scattering. The scattered intensity of a given reflection is proportional to the square of its crystallographic structure factor. For a monoclinic pseudocubic perovskite, the structure factors at the transition-metal K edge for the $(\frac{h}{2}\frac{k}{2}\frac{l}{2})$ and $(\frac{h}{2}\frac{\bar{k}}{2}\frac{l}{2})$ reflections with odd h, k, and l are given by $F_{\frac{hkl}{222}}(\mathbf{q}, E) = A(\mathbf{q}) + \sum_{j=1}^{4}(-1)^j f_j^r(E)$ and $F_{\frac{h\bar{k}l}{222}}(\mathbf{q}, E) = B(\mathbf{q}) + \sum_{j=1}^{4}(-1)^{j+1} f_j^r(E)$, where $\mathbf{q}$ and E are the x-ray momentum vector and energy, respectively, A and B are the contributions from atoms that do not resonate at the absorption edge under study, f_j^r is the resonant scattering factor of the jth transition-metal site in the monoclinic unit cell, and all sites represented by even (odd) j have nearest neighbor transition-metal sites represented by odd (even) j [39,40]. These equations show that if the charges on each of the cobalt sites in the $LaCoO_3$ film on $SrTiO_3$ are different from those of their nearest neighbors, f_j^r for even j will be different from f_j^r for odd j, and the cobalt ion contributions to these two reflections will be equal and opposite. This effect is observed in the resonant spectra shown in Fig. 3(a), where the peaks and valleys of the Co K-edge resonant intensity of the $(\frac{1}{2}\frac{1}{2}\frac{7}{2})$ become inverted with respect to those of the $(\frac{1}{2}\frac{\bar{1}}{2}\frac{7}{2})$, indicating the presence of cobalt ions with two different charges ordered in a rocksalt-type arrangement, as

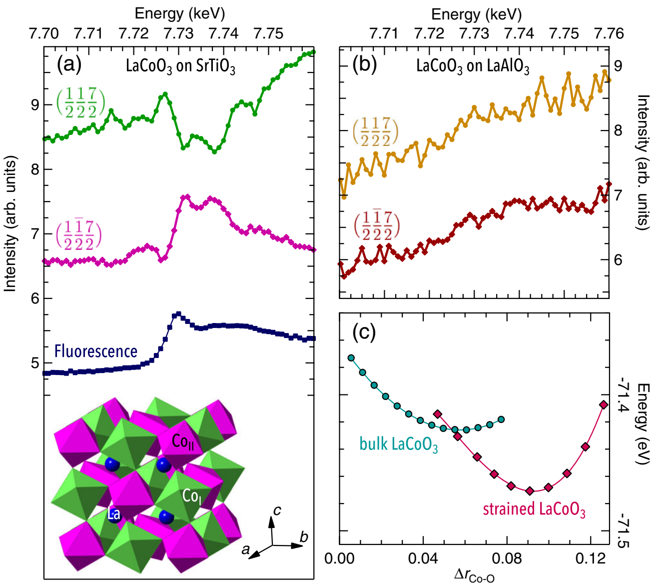

FIG. 3. The Co K-edge resonant intensity of the $(\frac{1}{2}\frac{1}{2}\frac{7}{2})$ and $(\frac{1}{2}\frac{\bar{1}}{2}\frac{7}{2})$ film reflections from (a) $LaCoO_3$ on $SrTiO_3$ and (b) $LaCoO_3$ on $LaAlO_3$. The total fluorescence yield from $LaCoO_3$ on $SrTiO_3$ is also shown. [Inset to (a)] A schematic of the crystal structure of the $LaCoO_3$ film on $SrTiO_3$. (c) The calculated total energy as a function of $\Delta r_{\text{Co–O}}$.

illustrated in the inset to Fig. 3(a) [41]. In contrast, variation in the resonant intensity is not observed at the $(\frac{1}{2}\frac{1}{2}\frac{7}{2})$ and $(\frac{1}{2}\frac{\bar{1}}{2}\frac{7}{2})$ reflections from the $LaCoO_3$ film on $LaAlO_3$ [Fig. 3(b)] [41]. Thus cobalt does not contribute to the structure factor at these reflections in this film.

The pattern of cobalt charge order identified in $LaCoO_3$ on $SrTiO_3$ by x-ray scattering is precisely that of the spin-state order predicted to occur in $LaCoO_3$ films under tensile strain by computational calculations, which indicate the occupation of the Co $3d$ derived e_g and t_{2g} orbitals alternates such that HS and LS Co^{3+} ions form a rocksalt-type arrangement [11,12,42]. Additionally, our calculations link charge and spin-state order in $LaCoO_3$, showing a difference of 0.17 $3d$ electrons between LS and HS cobalt ions. Thus, the experimentally observed charge order originates in concert with spin-state order. Furthermore, DFT + U calculations confirm that this arrangement of cobalt spin states leads to ferromagnetism. Indeed, the $LaCoO_3$ film on $SrTiO_3$ shows a ferromagnetic transition, and charge order is present therein, whereas both charge order and ferromagnetism are absent in $LaCoO_3$ on $LaAlO_3$, consistent with the proposed relationship between charge order, spin-state order, and ferromagnetism.

In the paramagnetic phase of unstrained $LaCoO_3$, spin-state order results from cooperative oxygen displacements that modulate the volume of the cobalt-containing octahedra [19]. Thus, the spin-state order is dynamic. In contrast, charge order, and therefore spin-state order, are static in strained $LaCoO_3$. In the case of a fluctuating electron configuration, the charge would be, on average, equal at all of the Co sites on the timescale of the measurement, and the observed differences in resonant diffraction at different half-order reflections would be absent. In addition, both the observation of the $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ film reflection and our DFT + U calculations indicate a variation in the octahedral volume between Co sites in strained $LaCoO_3$. In Fig. 3(c), the calculated total energy is shown as a function of the difference in in-plane Co─O bond length between different Co sites ($\Delta r_{\text{Co–O}}$) for both strained and bulk $LaCoO_3$ [43]. In both cases, a finite difference minimizes the energy. However, the minimum in the total-energy curve of bulk $LaCoO_3$ is shallower and occurs at smaller $\Delta r_{\text{Co–O}}$ than that of strained $LaCoO_3$, consistent with the dynamic nature of spin-state order in bulk $LaCoO_3$. Under tensile strain, which induces a difference between in-plane and out-of-plane Co─O bond lengths and increases the octahedral volume, the minimum deepens. Thus, in addition to the anticipated induction of octahedral distortions, strain stabilizes the cooperative oxygen displacements found in bulk $LaCoO_3$ creating a static octahedral breathing distortion. The cobalt spin state couples to the octahedral volume, and in essence, tensile strain freezes in the spin-state order found in the bulk paramagnetic phase.

In the ordered HS-LS Co^{3+} rocksalt-type arrangement, superexchange interactions, both dependent upon and independent of electron-configuration fluctuation, have been proposed as possible microscopic mechanisms leading to ferromagnetism [11,12,44]. The results presented herein demonstrate that the latter model underlies emergent ferromagnetic order. In the case of a static electron configuration, exchange reliant upon electron-configuration fluctuation cannot take place. For the static spin-state arrangement, ferromagnetism results from 90° superexchange interactions between next nearest neighbor HS cobalt ions mediated by the LS cobalt ions that separate them [11].

A ferromagnetic transition occurs at ~80 K in $LaCoO_3$, in spite of a temperature-independent electronic structure [6] and a significantly reduced thermal expansion coefficient imposed by $SrTiO_3$ [45]. Furthermore, the spin-state concentration is constant in epitaxial $LaCoO_3$ between 50 and 450 K [46]. The results presented herein lend clarity to this apparent contradiction. Strain locks in the electron-configuration order needed for a ferromagnetic state to persist as the ground state of the system, allowing a transition to long-range magnetic order as thermal energy is reduced. This is markedly different from the spin-state transitions found in bulk $LaCoO_3$.

In summary, we present evidence that strain induced structural distortions solidify the LS-HS ordered electron configuration, precipitating the emergence of ferromagnetic order. In combination with a change in symmetry, expansion of the in-plane lattice alters the energy landscape such that an ordered arrangement of two unique Co local environments is favored. The dimensions of the oxygen octahedra couple directly with the local spin state, and charge order emerges concurrently. Through coupling of the lattice to charge and spin, epitaxial strain alters the delicate balance between these parameters, stabilizing a new magnetic ground state with long-range order. Thus, the tendency for an ordered arrangement of two unique local environments about the ions on which correlated electrons reside is critical in bringing about a change in the magnetic phase. This phenomenon may play a role in spin-state and magnetic-phase transitions, regardless of stimulus, in many other correlated-electron systems.

We acknowledge S. Zohar for helpful discussions. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. DOE Office of Science by Argonne National Laboratory (ANL), was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357. H. P. and R. N. acknowledge support of start-up funding from UIC and ANL (by the U.S. DOE Office of Science program). We gratefully acknowledge the computing resources provided on Blues, a high-performance computing cluster operated by the Laboratory Computing Resource Center at ANL. Additional support from the National Institute of Standards and Technology (NIST) is also acknowledged. J. X. M. and J. S. are supported by DOE BES Award No. DEFG02-07ER46351.

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[*] sterbinsky@anl.gov

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[41] In order to obtain the elastic component of the resonant Co K-edge intensity at a given reflection, the background intensity was recorded with an x-ray momentum vector that did not satisfy a diffraction condition and subtracted from the intensity measured at the reflection. The background is dominated by Co $K\alpha,\beta$ fluorescence.

[42] Because of the distortion of the oxygen octahedra, e_g and t_{2g} only approximate the actual Co $3d$ derived energy levels.

[43] The minimum-energy bulk structure is obtained by performing structural relaxation under HS-LS spin symmetry giving a finite Co─O bond-length difference. In any given octahedron, all Co─O bond lengths are equal. Structures with different $\Delta r_{\mathrm{Co-O}}$ are obtained by interpolation between the HS-LS solution and a purely LS solution with equal volume.

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