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Competing electronic ground states in $La_{1-x}Ca_xCoO_3$

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We present the results of a neutron powder-diffraction study on $La_{1-x}Ca_xCoO_3$. We show that, contrary to previous reports, a first-order structural transition $R\bar{3}c \rightarrow Pnma$ occurs as a function of both x and T. Spin-state transitions occur as a function of x, T as indicated by the changes in cell volume, with evidence of a macroscopically inhomogeneous spin-state mixture at $x=0.1$. The magnetic behavior generally parallels that of $La_{1-x}Sr_xCoO_3$, with evidence for both spin-glass behavior and ferromagnetism.

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I. INTRODUCTION

The growth of interest in the cobaltite perovskites $LaCoO_3$ and $La_{1-x}Sr_xCoO_3$ (LSCO) is in part due to the expectation that, in addition to the lattice, charge, and spin degrees of freedom found in many other transition-metal oxides, the cobalt oxides will also display a degree of freedom in the "spin state" at the cobalt site.[1–12]

The spin states of the d^6 Co^{3+} ion in octahedral symmetry can be described as low spin (LS) $t_{2g}^6 e_g^0$, intermediate spin (IS) $t_{2g}^5 e_g^1$ and high spin (HS) $t_{2g}^4 e_g^2$, and are favored by large crystal-field splitting, covalency, and exchange energy, respectively.[3,13] $LaCoO_3$ appears to adopt the LS state for $T/K<80$, with transitions on warming to configurations dominated by IS ($80 \leqslant T/K \leqslant 500$) and then the HS states ($T/K>500$). The IS state is expected to be Jahn-Teller (J-T) active; however, $LaCoO_3$ is rhombohedral at all temperatures, which precludes the presence of a static, coherent Jahn-Teller distortion. There is evidence for an incoherent, and/or dynamic J-T distortion from neutron pair-distribution analysis and fitting of the thermal expansion and magnetization.[1,2,12] For LnCoO$_3$ with Ln a small lanthanide, it has been reported that the structure having $Pnma$ symmetry is more stable, as is the LS state.[14–16]

In the LSCO system, studies to date have concentrated on the observed competition between ferromagnetism and spin-glass behavior. Doping with Sr^{2+} introduces holes into the Co-O network. It also introduces size variance on the A site, which has been shown to affect the properties of oxides, and is an added complication in studies of $LaCoO_3$ derivatives.[17] La^{3+} and Ca^{2+} have very similar ionic radii (1.36, 1.34 Å, repectively[18]), but there has been surprisingly little study of the $La_{1-x}Ca_xCoO_3$ (LCCO) system.[19–23] Studies of bulk samples have suggested that there are no major differences from the Sr-doped system: all materials are reportedly rhombohedral for all levels of doping, and ferromagnetism is observed in both systems, with the Curie temperature being lower in the Ca-doped materials at a fixed doping level.

In this paper we show that LCCO differs significantly from LSCO. Neutron powder-diffraction shows that, contrary to previous reports, these materials are not invariably rhombohedral ($R\bar{3}c$), but that an orthorhombic ($Pnma$) phase exists at low temperatures for $x \geqslant 0.15$. From analysis of thermal-expansion data, we argue that LCCO exhibits spin state transitions as a function of both x and T and that a crossover from LS to IS stability occurs for $x \approx 0.1$. This crossover composition reflects a macroscopically inhomogeneous spin-state distribution extending into the phase diagram well beyond that proposed for the LSCO system.[24]

II. RESULTS

Polycrystalline samples of LCCO ($x=0.02,0.1,0.15,0.2$) were prepared using standard solid-state methods. We were unable to prepare single-phase materials for $x>0.2$. Neutron powder-diffraction patterns were collected using the Special Environment Powder-Diffractometer at the Intense Pulsed Neutron Source at Argonne National Laboratory; magnetic data were collected using a Quantum Design PPMS.

As shown in Fig. 1, neutron diffraction shows unequivocally that LCCO undergoes a structural phase transition $R\bar{3}c \rightarrow Pnma$ as a function of doping and temperature. This contrasts with LSCO which has been reported by numerous authors to adopt $R\bar{3}c$ symmetry at all measured temperatures (e.g., Ref. 1). A considerable region of coexistence between these phases is observed for $x=0.15$ and 0.2, consistent with the first-order nature of this phase transition. In the case of $x=0.15$ both $R\bar{3}c$ and $Pnma$ phases are found even at 12 K. The reduced symmetry of the orthorhombic phase can in principle allow a coherent ordering of Jahn-Teller distorted octahedra, as is observed in $LaMnO_3$. However, our mea-

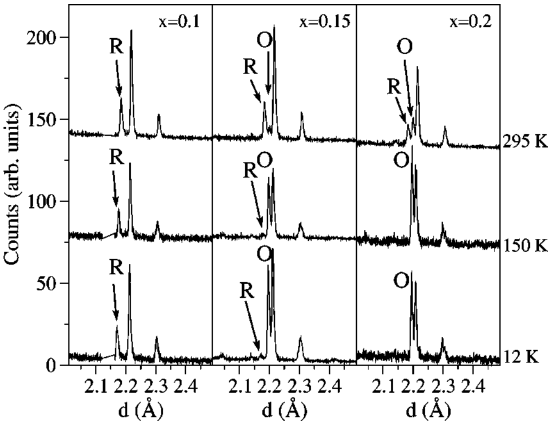

FIG. 1. Neutron powder-diffraction patterns collected as a function of temperature for $La_{1-x}Ca_xCoO_3$. For the $x=0.1$ sample the vanadium reflection at 2.13 Å due to the sample container has been excluded. R=rhombohedral, O=orthorhombic.

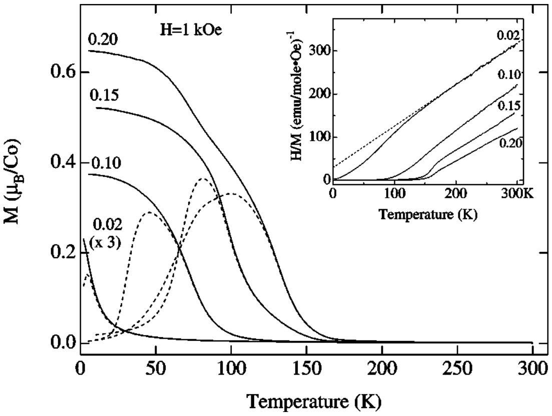

FIG. 2. $M(T)$ for $La_{1-x}Ca_xCoO_3$ collected in zero-field cooled (- - -) and field-cooled (—) modes, respectively. The inset shows $1/\chi$ as a function of T, the straight line is a Curie-Weiss fit to the $x=0.02$ data in the range $200 \leqslant T/K \leqslant 300$.

TABLE I. Parameters from Grüneisen-Einstein, Curie-Weiss fits and magnetization measurements. Data for $x=0$ taken from Ref. 1. μ_{eff} calculated assuming $g=2$. See text for further details.

x	V_0 ($Å^3$)	T_E (K)	$\alpha \times 10^{-3}$	θ_W (K)	μ_{eff} (μ_B/Co)	$M_{5\text{ T},10\text{ K}}$ (μ_B/Co)	$M_{10\text{ K}}$[a] (μ_B/Co)
0	110.4	50.5	1.61	-200			
0.02	110.4	64.8	1.84	-15	2.79	0.24	
0.1	110.8	246.9	6.85	94	2.72	0.58	0.61(4)
0.15	111.0	443.7	12.21	124	2.98	0.99	1.12(2)
0.2	110.6	445.5	13.4	140	3.26	1.18	1.17(2)

[a] Derived from neutron powder diffraction.

surements on the $x=0.15$, 0.2 samples indicate that all Co-O bond lengths are equivalent within 2 e.s.d.s. Resistivity data indicate that for all samples $d\rho/dT$ is negative, with the resistivity decreasing by a factor of ca. 100 between $x=0.1$ and $x=0.2$. It is thus possible that the $x \geqslant 0.15$ samples are sufficiently metallic such that the expected Jahn-Teller distortion is suppressed due to high electron mobility. In any event, the lack of a coherent Jahn-Teller distortion reinforces the conclusion that the $R\bar{3}c \rightarrow Pnma$ phase transition is of a steric rather than an electronic origin.

The magnetic behavior of LSCO has been discussed by several authors as evolving from a spin-glass regime ($0<x<0.18$) to a cluster-glass or ferromagnetic (FM) state ($0.18<x<0.5$).[7–9] Our data indicate that the LCCO system parallels LSCO, with mixed glassy and ferromagnetic contributions. Figure 2 shows zero-field-cooled (ZFC) and field-cooled (FC) $M(T)$ data taken on warming in $H_{meas}=1$ kOe. A pronounced increase in M signaling ferromagnetism is observed for $x \geqslant 0.1$. For $x \geqslant 0.1$, T_C increases monotonically with x, in generally good agreement with reports from Taguchi *et al.* and Muta *et al.*[19,23] The latter authors argued that for the low-x regime such magnetic behavior indicates either long-range FM or a spin-glass regime. Our neutron-diffraction data show increased intensity in Bragg reflections below T_C, unequivocally demonstrating long-range FM, albeit with a saturation moment markedly reduced from that predicted for a uniform, ordered IS Co^{3+} state (Table I). Thus, for $x \geqslant 0.1$, a significant fraction of the sample adopts a FM ground state in zero field. This parallels the Sr-doped series, in which magnetic Bragg reflections were also observed for a 10%-doped powder, but not an 8%-doped single crystal.[8,10]

For all samples, ZFC and FC curves diverge below T_C, with the appearance of a peak in the ZFC data. Such irreversibilities have been attributed to spin-glass formation in the LSCO system.[9] However, Kumar *et al.* and Ganguly *et al.* have recently suggested that such peaks reflect a coercive field, $H_C > H_{meas}$.[25,26] Magnetization measurements on our LCCO samples indicate a pronounced H_C at 5 K (e.g., $H_C=7$ kOe for $x=0.2$), and we believe this offers the simplest explanation for the pronounced ZFC-FC divergence. Nonetheless, for all samples in our study we observe no saturation of M at 5 K for fields as high as 7 T, and we find a pronounced ω dependence on $\chi'(T)$ spanning the maximum. Both observations are consistent with a fraction of the sample being in a glassy state. Both Nam *et al.* and Leighton *et al.* have recently explored the coexistence of glassy and ferromagnetic components in the LSCO system.[27,28] It is likely that a similar inhomogeneous state exists in LCCO as well. Unlike the behavior observed in LSCO by Leighton *et al.*, however, the irreversibility in LCCO samples does not extend to temperatures far above the maximum.

Plots of $1/\chi$ versus T (inset, Fig. 2) show linear behavior above ca. 200 K.[29] With the exception of $x=0.02$, θ_W agrees well with the T_C determined by neutron diffraction (e.g., $x=0.2$, $\theta_W=140$ K, $T_C \approx 125$ K). μ_{eff} values in the range 2.9–3.2 μ_B/Co are consistent with reports that Co ions adopt an IS state in this temperature regime in LSCO and LCCO.[7,8,23] Unfortunately, from these data alone it is impossible to determine uniquely the spin state of Co^{3+} without certain assumptions about the spin state of Co^{4+}, for which considerable controversy abounds.[8,9,13] We note however that analysis of μ_{eff} using a HS Co^{4+} ion leads to an imaginary value of **S** for Co^{3+} at $x=0.1$, excluding the HS state of Co^{4+} invoked by Itoh *et al.*[9]

$\theta_W=-31$ K for the $x=0.02$ sample implies antiferromagnetic (AFM) interactions in the high-temperature limit, but neutron diffraction shows no AFM superlattice reflections at any temperature. Nor do we observe any FM contribution to neutron scattering as low as 10 K.[30] Nonetheless, a pronounced deviation from linearity in $1/\chi$ versus T (Fig. 2, inset), a ZFC-FC irreversibility, and a pronounced hysteresis at 2 K ($H_C=1.4$ kOe, $M_{2\text{ K},7\text{ T}}=0.3\mu_B$/Co) all indicate FM character in this nominally 2% Co^{4+} sample as well. In LSCO θ_W increases rapidly with x, but we can find no report of hysteresis for $x \approx 0.02$.[7]

We now turn to the question of spin-state transitions. Unit-cell volumes provide a marker for spin-state transitions because the Co-O bond length responds to a variable population of e_g antibonding orbitals. In a recent study, Radaelli *et al.* have analyzed the thermal expansion of $LaCoO_3$ in terms of contributions from phonons, spin-state transitions, and oxygen nonstoichiometry.[1] A similar analysis undertaken here for LCCO shows evidence of two types of crossover behavior: a doping induced crossover at low T and a ther-

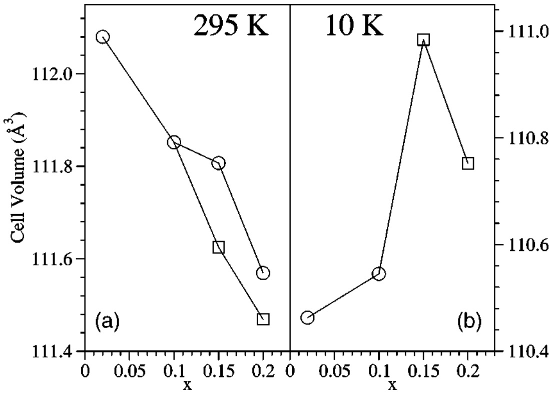

FIG. 3. (a) Cell volume at room temperature and (b) at 10 K for the rhombohedral (○) and orthorhombic (□) samples as a function of x. Error bars are smaller than the symbols. See text for further details.

mally induced crossover for $x<0.1$. These two crossovers can be ascribed to a spin-state transition from the $\mathbf{S}=0$ to $\mathbf{S}\neq 0$ electronic configurations at the Co^{3+} sites with increasing x,T. Additionally, the data suggest that the $x=0.1$ sample separates regions of LS and IS ground-state predominance, with both spin states preserved to low temperature at this composition.

Figure 3 shows the rhombohedral cell volume, V, as a function of doping at 295 K and at 10 K. At 295 K, V decreases monotonically with x, as expected by the substitution of Co^{4+} for Co^{3+} [$rCo^{3+}=0.545$ (LS), 0.61 (HS), $rCo^{4+}=0.53$ Å (Ref. 18)]. At 10 K, however, a distinctly different x-dependence is observed: V increases for $0<x<0.15$, then decreases on further Ca addition. Although the system becomes FM at $x\approx 0.1$, the magnitude of the volume change ($\Delta V/V\approx 0.5\%$ from $x=0$ to $x=0.15$) renders magnetostriction an unlikely explanation. We suggest that the different behavior reflects an average Co^{3+} spin state (and hence unit-cell volume) that varies smoothly with x at 295 K but not at 10 K.

The temperature dependence of V adds additional weight to this hypothesis. Figure 4(a) shows that on cooling, the $x=0.02$ cell volume crosses below that of samples with $x\geqslant 0.1$ at $T\approx 80$ K, reversing the trend seen at 295 K. The "anomalous" behavior of the $x=0.02$ sample is qualitatively similar to that of $LaCoO_3$ itself. The introduction of Co^{4+} may result in formation of IS Co^{3+} in its immediate vicinity, as has been suggested in LSCO.[7,8] A fraction of the remaining LS Co^{3+} located far from the Co^{4+} sites are thermally excited to the IS state. This effect will be most pronounced in samples that contain a large fraction of LS Co^{3+} at base temperature. Thus, the thermal-expansion data qualitatively indicate that Co^{3+} in $x=0.02$, with its dramatic increase in V for $T>40$ K, will be predominantly LS at base temperature, while Co^{3+} in samples $x\geqslant 0.1$ will be predominantly $\mathbf{S}>0$.

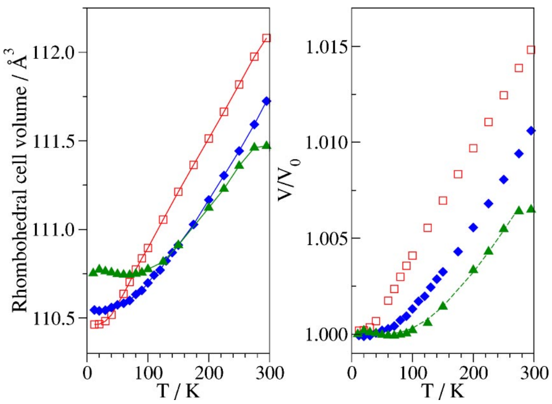

FIG. 4. (a) Rhombohedral cell volume and (b) $(V/V_0)(T)$ for $x=0.02$ (□), $x=0.1$ (♦), and $x=0.2$ (▲). Lines in (a) are to guide the eye; the dashed line in (b) is a fit (see text).

This discussion can be put on a more quantitative footing by fitting the thermal-expansion data with a Grüneisen-Einstein (G-E) model[31] that captures the phonon contribution[32] to $V(T)$. Extracted parameters are collected in Table I, and a representative fit to the $x=0.2$ data is shown in Fig. 4(b). Two regimes of parameters are found: $x<0.1$ and $x>0.1$.[33] For $x>0.1$, $T_E\approx 440$ K and $\alpha\approx 0.012$. These values can be compared to those proposed by Radaelli[34] for the phonon contribution to $V(T)$ for $LaCoO_3$: $T_E=423.34$ K and $\alpha=6.94\times 10^{-3}$. We thus propose that for $x>0.1$ the majority of Co^{3+} ions are in the IS state even at 10 K, giving a $V(T)$ that can be satisfactorily understood solely on the basis of phonons. For $x=0.02$, although the data can be fit, physically unrealistic parameters are obtained that are artifacts of the anomalous thermal expansion. Following Radaelli, we suggest that this sample has a marked contribution from electronic excitations as well as phonons, which signifies a majority LS configuration at 10 K.

The case of $x=0.1$ presents a crossover composition for which we speculate an inhomogeneous mixture of spin configurations, with both LS and IS preserved to low temperature. Note in Fig. 3 that at 10 K the volumes of $x\geqslant 0.1$ are greater than that of $x=0.02$ despite the larger Co^{4+} concentration in the former. This suggests that the CoO_6 octahedra in the $x\geqslant 0.1$ samples are, on average, in a higher spin state than those in $x=0.02$ at 10 K. As shown in Fig. 4(b), $V(T)/V_0$ for $x=0.1$ interpolates between the $x=0.02$, $x=0.2$ curves, indicating that the average spin state in the

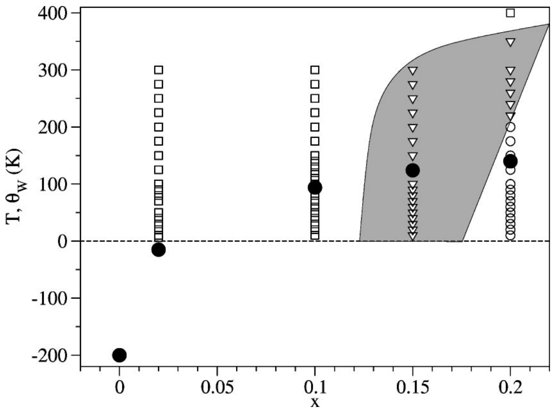

FIG. 5. Schematic phase diagram of $La_{1-x}Ca_xCoO_3$ derived from neutron powder diffraction. □ indicate $R\bar{3}c$, ○ $Pnma$, and ▽ the mixed regime. ● indicates θ_W. The grey area represents this mixed phase regime.

$x=0.1$ material is intermediate between those in $x=0.02$, 0.2 and thus implies a mixture of LS and IS in this composition at 10 K. A fit to the $x=0.1$ data, while qualitatively acceptable, yields parameters ($T_E=246.9$ K, $\alpha=6.85\times10^{-3}$) that lie between those extracted from the endpoint compositions. A change of slope in $V(x)$ is observed at $x\approx0.1$. This slope change may reflect a rapid increase in the population of the higher spin-state Co^{3+} ions from doping concentrations above this level. We thus hypothesize that at 10 K the $x=0.02$ sample is predominantly LS, the $x\geqslant0.15$ sample predominantly IS, and the $x=0.1$ sample a mixture with a significant fraction of both LS and IS. Assuming that for $T/K\leqslant80$, $x=0.0$ is 100% LS and that $x=0.2$ is fully IS, it is possible in principle to extract an estimate of the ratio LS:IS from these data. Attempts to fit the data using a linear combination of two G-E terms, although yielding a significantly better fit, were troubled by a shallow minimum for the least-squares fit. Nonetheless, the qualitative picture of a macroscopically inhomogeneous IS-LS mixture appears to be appropriate.

In summary, LCCO shares many features with LSCO, yet exhibits marked differences as well. We present our findings as a phase diagram in Fig. 5. With evidence for both long-range ferromagnetism and glassiness, LCCO closely parallels the behavior reported by numerous authors for LSCO. Likewise, there is evidence in both systems of a rapid destabilization of the LS state with doping. However, the Ca-doped system undergoes a first-order structural phase transition into orthorhombic symmetry for $x>0.1$. Thermal-expansion data indicate that at base temperature there is a crossover in the stability of the electronic ground state at $x\approx0.1$. This is considerably deeper into the phase diagram than that observed in LSCO. Finally, it is worth commenting that the assignment of the nonzero spin state to IS is far from firmly established. Indeed, the lack of a long-range ordered Jahn-Teller distortion in the orthorhombic phase is difficult to reconcile with an IS Co^{3+}. Nonetheless, from our data there is considerable evidence from both magnetic and thermal-expansion data for the presence of a macroscopically inhomogeneous distribution of spin states. Like LSCO it is probable that this inhomogeneous mixture is the origin of the glassy magnetism.

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[1] P.G. Radaelli and S.-W. Cheong, Phys. Rev. B **66**, 094408 (2002).

[2] C. Zobel, M. Kriener, D. Bruns, J. Baier, M. Gruninger, T. Lorenz, P. Reutler, and A. Revcolevschi, Phys. Rev. B **66**, 020402 (2002).

[3] M.A. Korotin, S.Y. Ezhov, I.V. Solovyev, V.I. Anisnmov, D.I. Khomskii, and G.A. Sawatzky, Phys. Rev. B **54**, 5309 (1996).

[4] S. Stølen, F. Grønvold, H. Brinks, T. Atake, and H. Mori, Phys. Rev. B **55**, 14 103 (1997).

[5] S. Xu, Y. Moritomo, K. Mori, T. Kamiyama, T. Saitoh, and A. Nakamura, J. Phys. Soc. Jpn. **70**, 3296 (2001).

[6] K. Asai, A. Yoneda, O. Yokokura, J.M. Tranquada, G. Shirane, and K. Kohn, J. Phys. Soc. Jpn. **67**, 290 (1998).

[7] M.A. Señarís-Rodríguez and J.B. Goodenough, J. Solid State Chem. **118**, 323 (1995).

[8] R. Caciuffo, D. Rinaldi, G. Barucca, J. Mira, J. Rivas, M.A. Señarís-Rodríguez, P.G. Radaelli, D. Fiorani, and J.B. Goodenough, Phys. Rev. B **59**, 1068 (1999).

[9] M. Itoh, I. Natori, S. Kubota, and K. Motoya, J. Phys. Soc. Jpn. **63**, 1486 (1994).

[10] K. Asai, O. Yokokura, N. Nishimori, H. Chou, J.M. Tranquada, G. Shirane, S. Higuchi, Y. Okajima, and K. Kohn, Phys. Rev. B **50**, 3025 (1994).

[11] J. Okamoto, H. Miyauchi, T. Sekine, T. Shidara, T. Koide, K. Amemiya, A. Fujimori, T. Saitoh, A. Tanaka, Y. Takeda, and M. Takano, Phys. Rev. B **62**, 4455 (2000).

[12] D. Louca, J.L. Sarrao, J.D. Thompson, H. Roder, and G.H. Kwei, Phys. Rev. B **60**, 10 378 (1999).

[13] R.H. Potze, G.A. Sawatzky, and M. Abbate, Phys. Rev. B **51**, 11 501 (1995).

[14] M. Itoh, M. Mori, S. Yamaguchi, and Y. Tokura, Physica B **259-261**, 902 (1999).

[15] M. Itoh, J. Hashimoto, S. Yamaguchi, and Y. Tokura, Physica B **281-282**, 210 (2000).

[16] X. Liu and C.T. Prewitt, J. Phys. Chem. Solids **52**, 441 (1991).

[17] L.M. Rodriguez-Martinez and J.P. Attfield, Phys. Rev. B **58**, 2426 (1998).

[18] R.D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **32**, 751 (1976).

[19] H. Taguchi, M. Shimada, and M. Koizumi, J. Solid State Chem. **41**, 329 (1982).

[20] A.V. Samoilov, G. Beach, C.C. Fu, N.-C. Yeh, and R.P. Vasquez, Phys. Rev. B **57**, R14 032 (1998).

[21] C. Zock, L. Haupt, B.M. Todris, K. Asadov, E.A. Zavadskii, and T. Gron, J. Magn. Magn. Mater. **150**, 253 (1995).

[22] S.K. Tolpygo, I.G. Mikhailov, A.E. Morozovsky, S.K. Yushchenko, and S.M. Ryabchenko, Physica C **185-189**, 1097 (1991).

[23] K. Muta, Y. Kobayashi, and K. Asai, J. Phys. Soc. Jpn. **71**, 2784 (2002).

[24] S. Yamaguchi, Y. Okimoto, H. Taniguchi, and Y. Tokura, Phys. Rev. B **53**, R2926 (1996).

[25] R. Ganguly, I.K. Gopalakrishnan, and J.V. Yakhmi, Physica B **271**, 116 (1999).

[26] P.S.A. Kumar, P.A. Joy, and S.K. Date, J. Appl. Phys. **83**, 7375 (1998).

[27] D.N.H. Nam, R. Mathieu, P. Nordblad, N.V. Khiem, and N.X. Phuc, Phys. Rev. B **62**, 8989 (2000).

[28] W. Wu and C. Leighton, Phys. Rev. B **67**, 174408 (2003).

[29] Measurements to 1073 K for $x=0.02$ show no additional features

that might indicate spin-state transitions.

[30] However, we note that the magnetometry data of Fig. 2 indicate that any ordered moment is likely to fall below neutron-diffraction detection limits.

[31] The equation used is $V = V_0\{1 + \alpha[\coth(T_E/T) - 1]\}$, where V_0 is the extrapolated zero-temperature unit-cell volume, α is the linear coefficient of thermal expansion for $T \gg T_E$, and T_E is the Einstein temperature.

[32] Implicit to both this argument and that of Radaelli is that the phonon spectra of LS and IS Co^{3+} do not differ drastically.

[33] The data for the rhombohedral phase of $x = 0.15$ were poorly fit due to the small volume fraction of this phase. We thus do not consider these data in this discussion.

[34] These values were numerically extracted from a Debye-Grüneisen model fit given in Ref. 1.