Proximate electronic and magnetic phase transitions in $CaFe_3O_5$

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Electronic phase separation in lightly doped $CaFe_3O_5$ has been investigated through a variable temperature powder neutron diffraction study of $CaFe_{2.99}M_{0.01}O_5$ (M = Co, Mn) samples. This reveals a complex series of proximate phase transitions. Lattice strains resulting from the onset of charge order (CO) drive formation of a competing charge averaged (CA) phase that emerges at $T_{CA} = T_{CO} = 320$ K. The CA phase emerges as magnetically ordered but the long range spin ordering transition is limited by domain growth and so occurs at a slightly lower temperature ($T_{CA(m)} = 301$ K for both samples). Magnetic ordering in the CO phase is not directly coupled to the other transitions, but is nearby in temperature with $T_{CO(m)} = 290(1)$ and 292(1) K for M = Co and Mn samples. The remarkable coincidence of energy scales for the formation of two distinct electronic ground states with differing lattice strains and their long range spin orders thus results in electronic and magnetic phase separation through a series of thermally proximate phase transitions in lightly doped $CaFe_3O_5$.

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I. INTRODUCTION

Coupling of charge, orbital, and spin degrees of freedom to a transition metal oxide lattice results in many interesting ground states [1–3] and important examples are found in iron oxides having mixed Fe^{2+}/Fe^{3+} charges. Magnetite, Fe_3O_4, is ferrimagnetic below 850 K and undergoes the Verwey transition at 125 K leading to changes in structural, magnetic, electrical, and thermal properties [4,5]. A complex Fe^{2+}/Fe^{3+} charge ordering and Fe^{2+} t_{2g} orbital ordering arrangement is observed with shortening of some $Fe^{2+} - Fe^{3+}$ distances showing that the extra Fe^{2+} spin down t_{2g} electron is spread over linear $Fe^{3+} - Fe^{2+} - Fe^{3+}$ units termed "trimerons" [6]. The trimeron description of the ground state has been shown to be consistent with spectroscopic and other experimental observations and is supported by theoretical models [7]. Further new mixed valent iron oxides such as Fe_nO_{n+1} ($n = 4$ and 5) and Fe_mO_{m+2} ($m = 5$ and 7) have been discovered at high pressure in recent years [8], notably Fe_4O_5, which can be recovered to ambient conditions [9]. Fe_4O_5 adopts the orthorhombic *Cmcm* $Sr_2Tl_2O_5$-type structure with three crystallographically distinct Fe sites, two FeO_6 octahedral sites, and one trigonal prismatic site [Fig. 1(a)], and also has a Verwey-like transition with low-temperature spin, charge, and orbital orders [10]. Several MFe_3O_5 (M = Ca [11,12], Mn [13,14], Co [15], and Ni [16]) derivatives where Fe at the trigonal prismatic sites is replaced by other cations have also been investigated, amongst which $CaFe_3O_5$ is particularly noteworthy as it can display electronic and magnetic phase separation.

Stoichiometric $CaFe_3O_5$ adopts a charge, orbital, and trimeron ordered ground state, referred to hereafter as the charge ordered (CO) phase, and undergoes magnetic transitions to an incommensurate phase at 289 K that locks into a commensurate structure with a propagation vector $\boldsymbol{k}$ = (½ 0 0) at 281 K [Fig. 1(b)] [12]. However, slight deviations in stoichiometry result in phase separation as both the CO and a charge averaged (CA) phase are observed. The CA phase has a uniform average $Fe^{2.67+}$ charge across the distinct octahedral Fe sites, with no charge, orbital, or trimeron order observed, and has an antiferromagnetic $\boldsymbol{k}$ = (0 0 0) spin order, different to that of the CO phase [Fig. 1(c)], although weak ferromagnetism is also observed [12]. Phase separation was first reported in an off-stoichiometric $Ca_{0.96}Fe_{3.04}O_5$ sample, in which a mixture of 40% CA and 60% CO phases was discovered [11]. Subsequent exploration of doped $CaFe_{3-x}M_xO_5$ (M = Mn and Co) samples found phase separation for $0.05 < x < 0.10$ and only the CA ground state was stabilized at $x > 0.10$ [17]. The CA and CO phases appeared to share a common electronic and magnetic transition near 300 K in all segregated samples, leading to the proposal that strains from differences between the lattice parameters of the CA and CO phases (both of which retain orthorhombic *Cmcm* symmetry to lowest temperatures) results in their coupled coemergence on cooling. This highly unusual behavior contrasts with that seen in electronically phase separated manganites where the

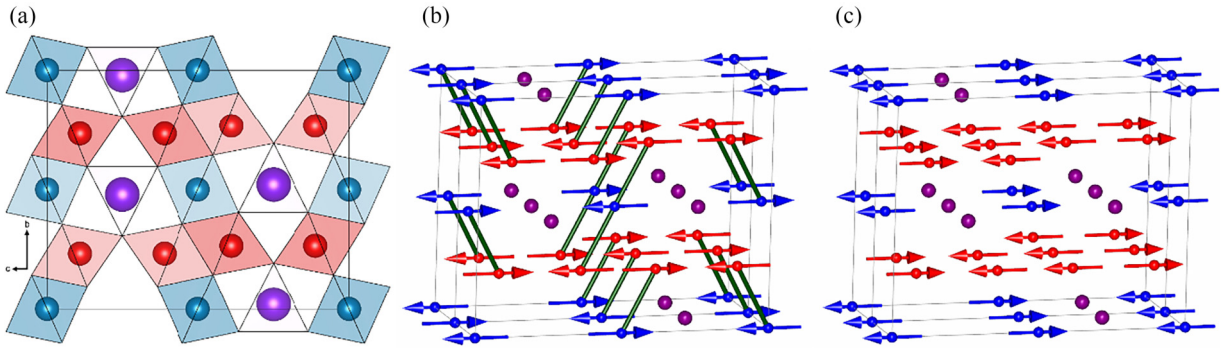

FIG. 1. (a) Projection of the $CaFe_3O_5$ structure showing Fe1 cations in blue, Fe_2 in red, and trigonal prismatic site in purple. (b) Magnetic structure of the CO phase with (½ 0 0) propagation vector; green lines show ferromagnetic order within trimerons. (c) Magnetic structure of the CA phase, with (0 0 0) propagation vector. Views (b) and (c) have ***a*/*b*/*c*** axes out-of-plane/vertical in-plane/horizontal in-plane. Figure adapted with permission from Ref. [17].

spin, charge, or orbital ordering temperatures of different ground states are often far apart [18,19].

To test whether the electronic and magnetic orders in phase-separated $CaFe_3O_5$ samples truly share a common transition temperature, we have explored two very lightly doped samples $CaFe_{2.99}M_{0.01}O_5$ (M = Co, Mn) by powder neutron diffraction over small temperature intervals in the present study. These dopants have different electronic effects as Mn^{2+}/Mn^{3+} charge states are formed in a similar ratio to Fe^{2+}/Fe^{3+} within the host structure, whereas Co has a greater tendency to form the +2 state [17]. However, the 0.33% doping levels are too small for any M-specific effects to be measured and comparison of results for the two samples is used to enable the intrinsic effects of light doping to be separated from any refinement artifacts.

II. EXPERIMENT

Samples of nominal composition $CaFe_{2.99}M_{0.01}O_5$ (M = Co, Mn), were prepared from stoichiometric amounts of $CaFe_2O_4$, Fe_2O_3, Fe, and MnO or CoO powder, as part of the work reported in Ref. [17]. Reactants were mixed and pressed into pellets before being sealed into evacuated quartz tubes and heated for 20 h at 1100 °C. $CaFe_2O_4$ was prepared using traditional solid state synthesis techniques with a 1:1 ratio of $CaCO_3$ and Fe_2O_3 pressed powders heated initially at 850 °C for 4 h, regrinding and repelletizing before a final heat at 1100 °C for 12 h. Phase confirmation was carried out using a Bruker D2 powder x-ray diffractometer. Magnetic susceptibility data are shown in the Supplemental Material [20].

Powder neutron diffraction (PND) patterns from 3 g samples of the two materials were collected on the Echidna high resolution powder diffractometer at the Australian Nuclear Science and Technology Organisation (ANSTO) OPAL reactor facility over a temperature range of 3 to 350 K for both samples, with a data acquisition time of 2 h per temperature point and a wavelength of 2.4395 Å. The PND data were collected using a closed-cycle refrigerator. The sample temperature was regulated by two independent DT-670 silicon diode sensors and heaters installed at the top and bottom of the sample, and temperature uniformity was facilitated by He exchange gas at a pressure ∼100 mbar in the sample space. Measurements were taken at 3 K, from 50 to 250 K in 50 K steps, and in 1 K increments between 280 and 300 K to focus on the critical region for the magnetic phase transitions. Data were also collected in 10 K increments between 300 and 350 K for the Mn sample and at 300 and 350 K for the Co sample.

III. REFINEMENT PROCEDURE

Rietveld fits to the $CaFe_{2.99}M_{0.01}O_5$ (M = Co, Mn) PND profiles were carried out using the FullProf Suite [21]. Initial fits to 350 K PND data confirmed that a single $CaFe_3O_5$-type nuclear phase with orthorhombic *Cmcm* symmetry is present in both M = Co and Mn samples. The contribution from ∼3% of a brownmillerite ($Ca_2Fe_2O_5$) type secondary phase was also included for all fits to each sample using published models for both the crystal and magnetic structures as $Ca_2Fe_2O_5$ has a Néel temperature of 725 K [22]. Additional magnetic diffraction peaks at 3 K confirmed long range electronic phase separation into the previously reported CA and CO phases for both samples. Hence Rietveld fits to 3 K and other low temperature profiles required four $CaFe_3O_5$-type phases, the nuclear structures for the CA and CO phases, which both have *Cmcm* symmetry but with different atomic and lattice parameters [11] and their magnetic structures which have respective ground state (0 0 0) and (½ 0 0) magnetic propagation vectors, where Fe coordinates and lattice parameters were constrained to the values for their nuclear phases.

Four physical transitions occur in phase-separated $CaFe_3O_5$ samples. The intrinsic electronic transition is for charge, orbital, and trimeron ordering to occur forming the charge ordered (CO) phase below T_{CO}. However, part of the sample does not undergo this electronic order and separates out into the distinct charge averaged (CA) phase below T_{CA}. Both CO and CA phases undergo long range spin orders with respective magnetic transition temperatures $T_{CO(m)}$ and $T_{CA(m)}$. In previous studies [11,17] all four transitions were reported as occurring simultaneously, i.e., $T_{CO} = T_{CA} = T_{CO(m)} = T_{CA(m)} \approx 300$ K. The present study aims to determine each transition temperature separately, but this is difficult because changes in the number of fitted $CaFe_3O_5$-type phases (from four to one between low and high temperatures) tend to lead to correlated discontinuities

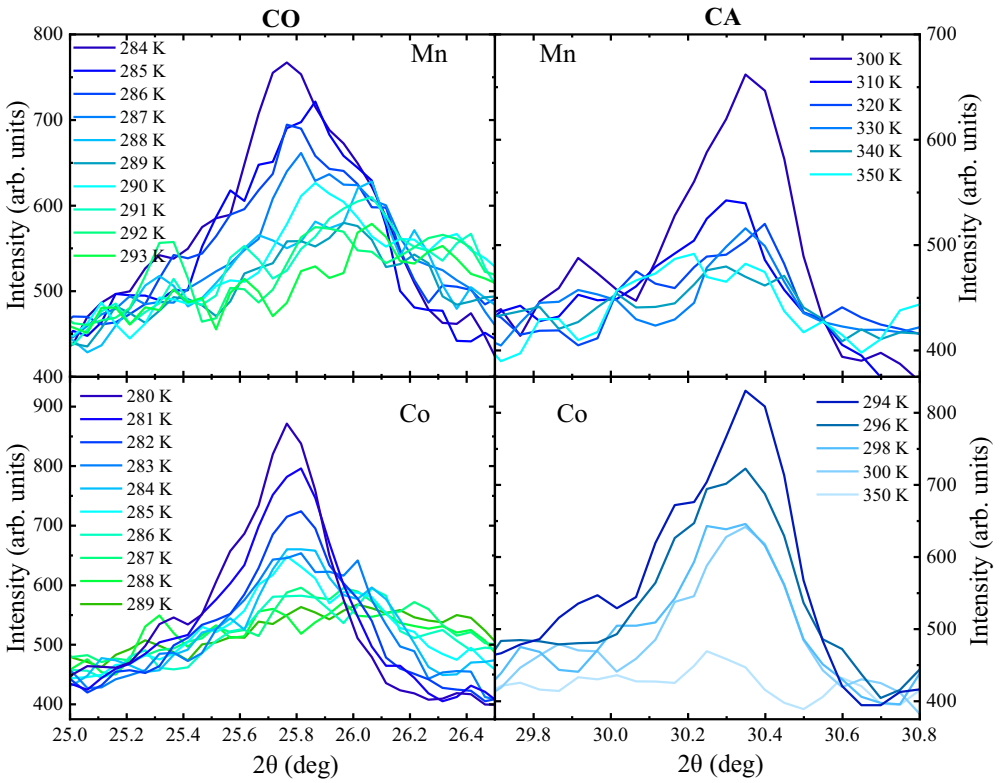

FIG. 2. Thermal evolution of the magnetic scattering from the (½ 0 1) CO (left) and (0 2 1) CA (right) reflections in $CaFe_{2.99}M_{0.01}O_5$ (M = Co, Mn). The raw PND data have been partially smoothed to improve visibility of the temperature evolution (wavelength = 2.4395 Å).

in refined parameters of other phases which may obscure the underlying transitions. Hence thermal changes in the PND data were used to establish upper temperature limits for inclusion of the refined phases as follows.

(1) Spin order in the CO phase is evidenced by an intense magnetic (½ 0 1) PND peak. This slightly shifts position on warming towards $T_{CO(m)}$ due to formation of an incommensurate magnetic phase (between 281 and 289 K in stoichiometric $CaFe_3O_5$) [12]. The lowest temperature point before emergence of the magnetic (½ 0 1) contribution is observed was taken as the initial value of $T_{CO(m)}$ to establish refinement limits, giving estimates of $T_{CO(m)} = 292$ K for the Mn sample and $T_{CO(m)} = 289$ K for the Co sample based on the data shown in Fig. 2.

(2) Spin order in the CA phase results in an intense (0 2 1) magnetic diffraction contribution. Appearance of diffuse scattering at this position is thus taken as a measure of where the CA phase separates out from the principal CO phase, i.e., T_{CA}. The lowest temperature point before emergence of additional scattering at the (0 2 1) Bragg position is observed in Fig. 2 was thus used to estimate $T_{CA} = 320$ K for the Mn sample. A nominal estimate of $T_{CA} = 300$ K was used for the Co sample as no data were collected between 300 and 350 K.

The above initial estimates of $T_{CO(m)}$ and T_{CA} were used to define the refinement regimes for the $CaFe_3O_5$-type phases in PND Rietveld fits. Four phases (nuclear and magnetic for both CO and CA phases) were used for fits to PND profiles at temperature $T < T_{CO(m)}$. Only the commensurate $\boldsymbol{k} = (½\ 0\ 0)$ spin structure was fitted for the magnetic CO phase as counting statistics on the weak satellite peaks were too poor to allow refinement of the reported incommensurate model near $T_{CO(m)}$. Three phases (nuclear CO and nuclear and magnetic CA) were fitted in the interval $T_{CO(m)} \leqslant T < T_{CA}$ and only a single nuclear phase was fitted for $T_{CA} \leqslant T$.

Site occupancies throughout were fixed at ideal values for stoichiometric $CaFe_3O_5$ as the M = Co and Mn contents of the $CaFe_{2.99}M_{0.01}O_5$ phases are too small to be detected in the PND fits. Representative profile plots (for four $CaFe_3O_5$-type phases at 3 K and one phase at 350 K) for the Mn-doped sample shown in Fig. 3 (and further plots in the Supplemental Material [20]) demonstrate that good fits are obtained. Separate orthorhombic cell parameters, magnetic moments (which were constrained to be of equal magnitude for the inequivalent Fe1 and Fe2 sites in each structure), and phase fractions for CA and CO phases were refined and results are shown in Figs. 4 and 5.

IV. MAGNETIC TRANSITIONS

Critical fits to the refined magnetic moments were used to give more accurate values of the spin ordering transition temperatures, assuming a continuous transition, as shown in Fig. 4. A previously reported empirical fitting function was used [23],

$$M = M_0 \tanh\left(W\left(\frac{T_c - T}{T_c}\right)^{\beta}\right) \Big/ \tanh(W), \qquad (1)$$

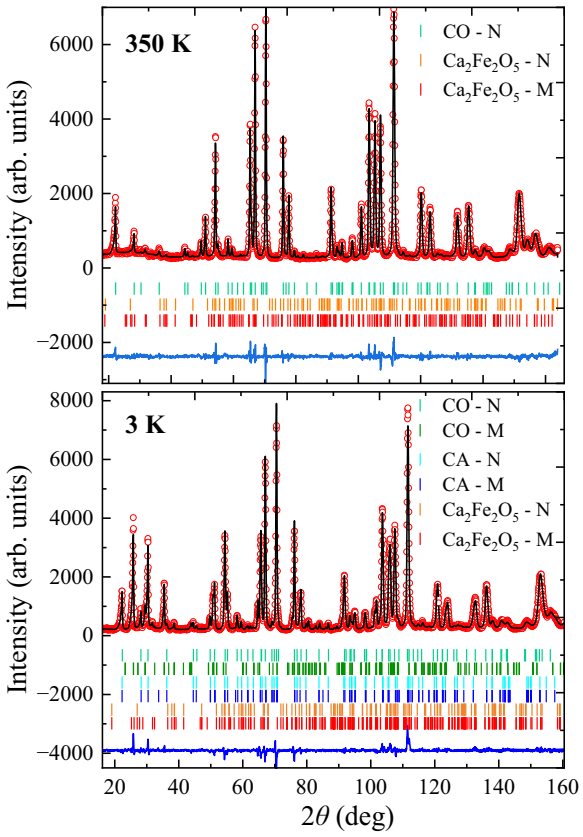

FIG. 3. Rietveld fits to PND profiles (wavelength = 2.4395 Å) for the $CaFe_{2.99}M_{0.01}O_5$ (M = Mn) sample at 350 K [profile and weighted profile R factors and reduced χ^2 are $R_p = 5.14\%$, $R_p = 6.50\%$, and $\chi^2 = 2.26$] and at 3 K [$R_p = 5.10\%$, $R_p = 6.51\%$, and $\chi^2 = 2.42$]. Bragg reflections are for the nuclear (N) and magnetic (M) contributions from $CaFe_3O_5$ [forming charge ordered (CO) and charge averaged (CA) phases at 3 K] and a trace of brownmillerite [2.5(2)% $Ca_2Fe_2O_5$] secondary phase.

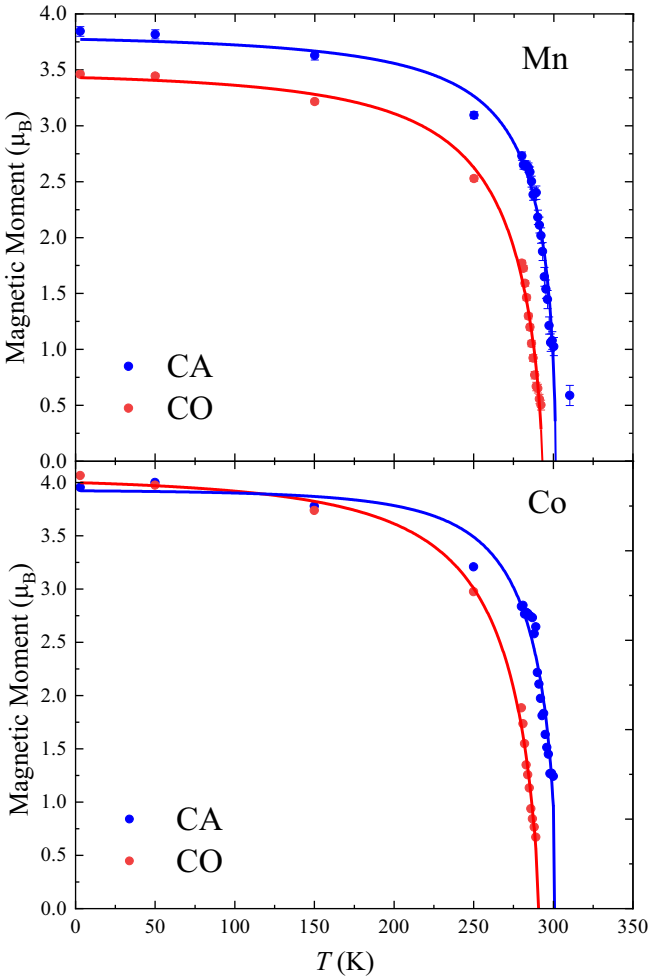

FIG. 4. Thermal evolution of the refined magnetic moments for the CO and CA phases in $CaFe_{2.99}M_{0.01}O_5$ for M = Mn (upper) and M = Co samples (lower). Lines show the fits of Eq. (1).

where M is magnetic moment, M_0 is the saturated moment, T_c is the magnetic transition temperature, W is a fitting parameter that allows for higher order terms to the critical expansion, and β is the critical exponent. Varying W and β independently gave critical exponent values of $\beta = 0.55(7)$ for CO magnetic transitions in both Mn and Co doped samples and $\beta = 0.43(6)$ for the Mn CA phase magnetic transition. These are within error of $\beta = 0.5$ for mean-field behavior which likely reflects averaging of a complex interaction background to the spin transitions as CO and CA phase proportions and also that lattice strains are thermally evolving over the critical region as described in the next section. CA phase magnetic moments in the Co-doped sample show an anomalous variation in the 280 to 289 K region due to refinement correlations with the CO magnetic phase which disappears above $T_{CO(m)} = 289$ K, so W and β could not be varied independently. The fit shown in Fig. 4 gave $\beta = 0.36(1)$ for a fixed $W = 2.2$ but this does not have any clear physical significance. The fits give saturated moments M_0 in the range 3.4 to 4.1 μ_B, which are typical for mixed Fe^{2+} ($S = 2$) - Fe^{3+} ($S = 5/2$) states in oxides, and demonstrate that CA and CO phase fractions are largely decorrelated from the magnitudes of the moments in the refinements.

The fitted $T_{CO(m)}$ values were 292(1) and 290(1) K for Mn and Co doped samples, respectively, in good agreement with the estimates of 292 and 289 K above based on observed appearance of magnetic peaks. These are also in agreement with the reported value of 289 K in stoichiometric $CaFe_3O_5$ [12]. Fitted $T_{CA(m)}$ temperatures of 301(1) for both Mn and Co doped samples are significantly greater than the $T_{CO(m)}$ values, demonstrating that long range spin ordering transitions in the CO and CA phases do not occur at identical temperatures, but are separated by ~10 K. It is also notable that the fitted $T_{CA(m)} = 301(1)$ for the Mn doped sample lies below $T_{CA} = 320$ K, where broad Bragg peaks overlying diffuse scattering evidence the upper limit of the CA phase. This likely indicates that long range spin ordering in the CA phase is suppressed by decreasing domain size and so the spin ordering transition $T_{CA(m)}$ lies below the disappearance of CA domains at T_{CA}. This could not be observed for the Co sample as no data were collected in the likely region of T_{CA} between 300 and 350 K. Overall, these observations thus demonstrate that the transitions in phase separated $CaFe_{2.99}M_{0.01}O_5$ (M = Co, Mn)

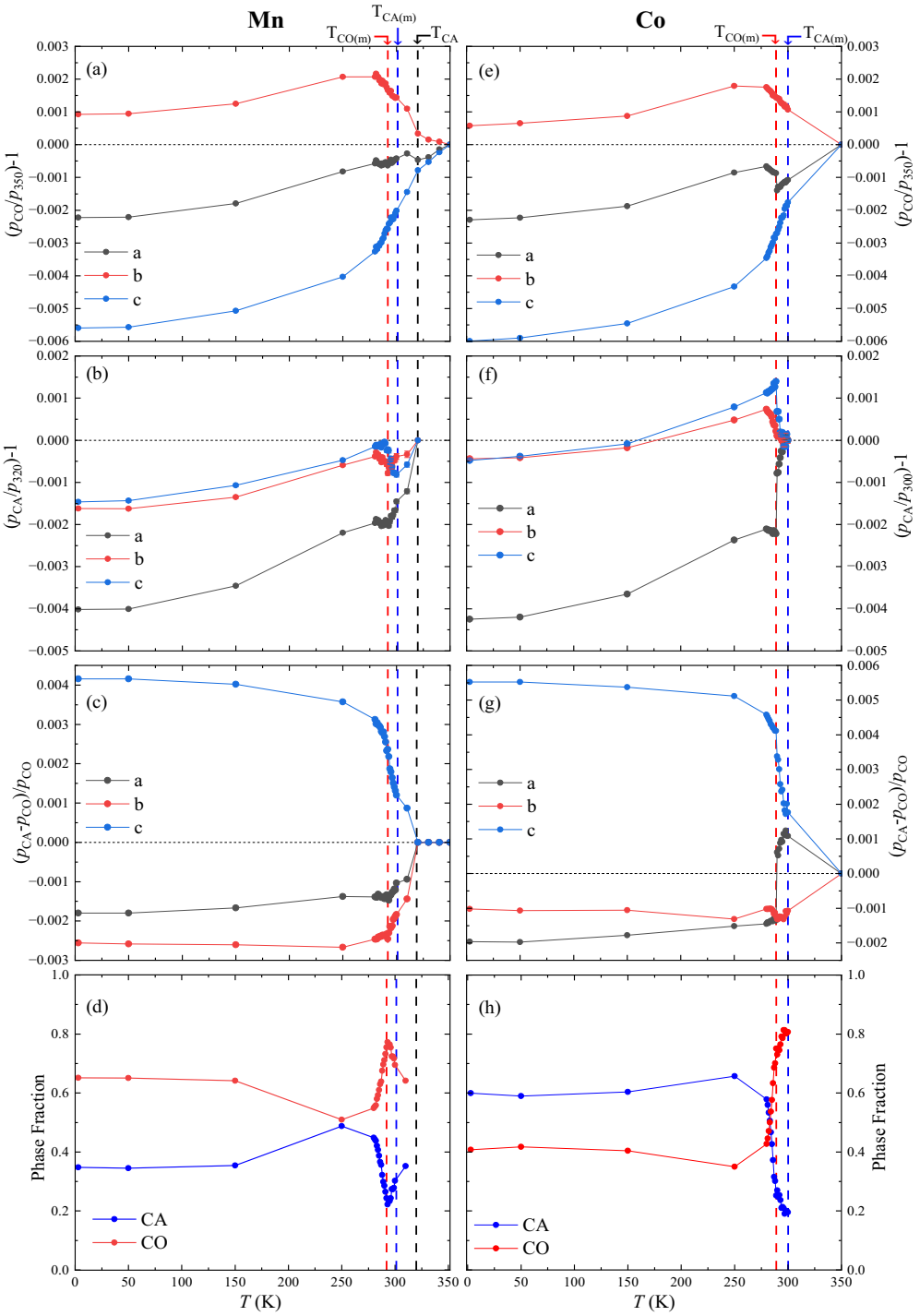

FIG. 5. Thermal evolution of the lattice strains for the orthorhombic *Cmcm* $CaFe_{2.99}M_{0.01}O_5$ CO and CA phases in (a)–(d) M = Mn and (e)–(h) M = Co samples. Phase transitions at $T_{CO(m)}$ and $T_{CA(m)}$ and at T_{CA} for the M = Mn sample are shown as dashed lines. (a) Lattice strains for the CO phase in the M = Mn sample normalized to 350 K values [$a_{350\ K} = 3.03048(5)$, $b_{350\ K} = 10.0064(1)$, and $c_{350\ K} = 12.6365(2)$ Å]. (b) Lattice strains for the CA phase in the M = Mn sample normalized to $T_{CA} = 320$ K values [$a_{320\ K} = 3.0268(1)$, $b_{320\ K} = 10.0029(7)$, and $c_{320\ K} = 12.6292(7)$ Å]. (c) Interphase strain between the CO and CA phases in the M = Mn sample. (d) Thermal evolution of CO and CA phase fractions in the M = Mn sample. (e) Lattice strains for the CO phase in the M = Co sample normalized to 350 K values [$a_{350\ K} = 3.03225(1)$, $b_{350\ K} = 10.01333(1)$, and $c_{350\ K} = 12.64538(2)$ Å]. (f) Lattice strains for the CA phase in the M = Co sample normalized to 300 K values [$a_{300\ K} = 3.0325(1)$, $b_{300\ K} = 10.0014(6)$, and $c_{300\ K} = 12.6253(6)$ Å]. (g) Interphase strain between the CO and CA phases within the M = Co sample. (h) Thermal evolution of CO and CA phase fractions in the M = Co sample.

samples do not coincide but are closely spaced in the sequence $T_{CO(m)} < T_{CA(m)} < T_{CA}$ with separations of 10–20 K between successive transitions.

V. PHASE PROPORTIONS AND LATTICE STRAINS

The refined relative CA and CO phase fractions in $CaFe_{2.99}M_{0.01}O_5$ (M = Co, Mn) shown in Fig. 5 demonstrate that the proportion of the CA phase which emerges below T_{CA} (= 320 K for the Mn-doped sample) increases to maximum values of 48(1)% for the Mn and 64(1)% for the Co sample near 250 K and decreases slightly on further cooling to 35(1)% CA in the Mn sample and 58(1)% in the Co sample at 3 K. The apparent decrease seen in the CA fraction in Fig. 5(d) on cooling from $T_{CA(m)}$ to $T_{CO(m)}$ in the Mn doped sample is attributed to refinement correlations as the effect is unphysical and is not seen for the Co sample in Fig. 5(h). This study thus demonstrates that as little as 0.33% Co or Mn doping is sufficient to stabilize substantial electronic phase separation and the differing CA/CO proportions in the two samples reveal sensitivity to different dopants even at this low doping level. This may reflect the different sizes of the dopants as Mn^{n+} and Co^{n+} cations are respectively larger and smaller than their Fe^{n+} counterparts and are found to substitute at different sites in MFe_3O_5 (M = Co, Mn) analog phases [14,15]. Specific lattice effects such as Jahn-Teller distortion of Mn^{3+} may also play a role.

Previous studies [11,17] have demonstrated that the electronic and magnetic orders in both $CaFe_3O_5$ phases are strongly coupled to the lattice resulting in macroscopic lattice strains that drive the phase separation. The thermal lattice parameter strains $\Delta p/p$ in the orthorhombic cell parameters ($p = a$, b, or c) of the CO and CA phases in each sample are shown as $[p/p(T_{max})] - 1$ by normalizing to the value at the highest observed temperature T_{max}, as presented in Fig. 5. Apparent discontinuities such as in a-parameter strains for the Co sample at $T_{CO(m)}$ seen in Figs. 5(e)–5(g) are likely refinement anomalies as the same strains evolve smoothly through the same transition for the Mn sample in Figs. 5(a)–5(c).

The differing strains of the CO and CA phases are driven primarily by shortening of Fe-Fe contacts across edge-sharing FeO_6 octahedra when their spins are ordered parallel in their magnetic phases, which allows delocalization of the minority spin t_{2g} electron between $t_{2g}^4 e_g^2$ Fe^{2+} and $t_{2g}^3 e_g^2$ Fe^{3+} states. In the CO phase this occurs within the trimeron units in the bc plane [Fig. 1(b)] leading to predominant shortening of the c axis on cooling in Figs. 5(a) and 5(e), while ferromagnetic chains parallel to the a axis [Fig. 1(c)] of the CA phase lead to a pronounced shortening of that parameter on cooling as seen in Figs. 5(b) and 5(f) and as reported in previous studies of $CaFe_3O_5$ phases [11,12,17].

The CO phases in both $CaFe_{2.99}M_{0.01}O_5$ (M = Co, Mn) samples behave similarly [Figs. 5(a) and 5(e)], showing a contraction in a and c while elongating b as the sample is cooled below the 350 K upper limit of measurements. Discontinuities in all CO lattice parameters are observed at 320 K for the Mn sample [Fig. 5(a)], which is significantly above the CO spin ordering temperature ($T_{CO(m)}$ = 292 K) and so is identified as the charge ordering transition temperature T_{CO}. This is corroborated by lattice parameter variations reported for undoped $CaFe_3O_5$ samples (where only the CO ground state was observed) where separate discontinuities are observed near 290 and 320 K [12]. Furthermore, the occurrence of distinct charge and magnetic ordering transitions for the CO phase of $CaFe_3O_5$ is in keeping with other mixed valent iron oxides. The relative magnitude of these phase transition temperatures varies as Fe_3O_4 and Fe_4O_5 both have $T_{CO} < T_m$ [10,24] but the sequence is reversed for $CaFe_3O_5$ and notably also for Fe_2BO_4 (Fe_2OBO_3), which has a similar orthorhombic crystal structure based on connected chains of edge-sharing FeO_6 octahedra and has T_m(= 155 K) < T_{CO}(= 315 K) [25,26].

The T_{CO} = 320 K transition in our Mn doped sample is coincident with emergence of the CA phase (derived above from the onset of diffuse CA-phase magnetic scattering) showing that these transitions are coupled, i.e., $T_{CA} = T_{CO}$ = 320 K. This is in keeping with the previous proposition [17] that lattice strains created by charge ordering in $CaFe_3O_5$ samples containing lattice inhomogeneities due to slight doping result in part of the sample separating out as the distinct CA phase. This is corroborated by the rapid emergence of lattice strain for the CA phases [Figs. 5(b) and 5(f)] on cooling below $T_{CA} \approx$ 320 K to $T_{CO(m)} \approx$ 290 K, and also by the interphase strains (p_{CA}/p_{CO})–1 in Figs. 5(c) and 5(g), which are comparable in magnitude to the strains within the individual CO and CA phases.

VI. DISCUSSION

The above results can be combined with those from previous studies [11,12,17] to give a consistent and more complete picture of the electronic and magnetic transitions and phase separation in $CaFe_{3-x}M_xO_5$ as follows.

(1) Very clean $CaFe_3O_5$ samples (with doping $x < 0.01$) undergo charge ordering at $T_{CO} \approx$ 320 K and magnetic order at $T_{CO(m)}$ = 289 K, with a further incommensurate to commensurate lock-in at 281 K [12]. These intrinsic values of T_{CO} and $T_{CO(m)}$ remain almost constant in doped, phase-separated samples.

(2) Highly doped $CaFe_{3-x}M_xO_5$ samples ($x > 0.1$ for M = Co, Mn) adopt only the charge averaged (CA) ground state with a long range magnetic transition at $T_{CA(m)} \approx$ 330 K [17]. There is no evidence for separate electronic and magnetic transitions in these samples, i.e., $T_{CA} = T_{CA(m)}$, so the lattice distortions associated with CA spin ordering may be described as a magnetoelastic coupling at the magnetic transition.

(3) When lightly doped $CaFe_{3-x}M_xO_5$ samples ($0.01 \leqslant x < 0.1$ for M = Co, Fe, and Mn, where the lower limit is demonstrated in the present study of $x = 0.01$, M = Co and Mn samples) undergo the charge ordering transition, the associated lattice strains drive part of the sample into the charge averaged state, so the emergence transition for the CA phase is at $T_{CA} = T_{CO}$ = 320 K. Phase separation is thus induced by even the slight inhomogeneities associated with doping levels as small as 0.33%. The emerging CA domains are below their intrinsic magnetic ordering temperature (≈330 K) but they are initially too small to support long range spin order, as evidenced by a broad Bragg peak overlying diffuse magnetic scattering seen below T_{CA}, so the transition as estimated by

critical fits is shifted to lower temperatures [$T_{CA(m)} = 301$ K for both $CaFe_{2.99}M_{0.01}O_5$ (M = Co, Mn) samples], where larger domains of the CA phase occupying 20–70% of the total sample are formed [17]. This is corroborated by previously reported results for a $CaFe_{2.90}Mn_{0.10}O_5$ sample where 90% of the sample converted to the CA phase and fitting of a critical function gave $T_{CA(m)} = 320.5$ K ($= T_{CA}$) [17]. The residual CO phase in the phase separated samples undergoes magnetic order at $T_{CO(m)} = 290$–292 K, essentially unchanged from the transition in clean $CaFe_3O_5$ at $T_{CO(m)} = 289$ K.

Hence the previously proposed description [11,17] of the electronic and magnetically ordered phases of doped $CaFe_3O_5$ coemerging at a single transition through mutual strain coupling has to be modified. The CO and CA phases do coemerge from a common transition, at $T_{CA} = T_{CO} = 320$ K in the present $CaFe_{2.99}M_{0.01}O_5$ (M = Co, Mn) samples, as evidenced by the lattice strains of both phases relative to the parent high temperature structure. T_{CA} lies below the intrinsic magnetic ordering temperature for the emerging CA phase so spin order is limited by the growth of domain size on cooling and this leads to varying $T_{CA(m)}$ values between 300 and 320 K for differently doped samples as measured by critical fits to the long range ordered moment. The magnetic transition of the CA phase is thus coupled to the emergence of the CA and CO phases with $T_{CA(m)} \leqslant T_{CA} = T_{CO} = 320$ K. However, the spin ordering temperature of the CO phase at $T_{CO(m)} = 289$ K does not appear to be coupled to the other transitions as it remains virtually constant across undoped and phase separated samples, although the 30 K separation between $T_{CO(m)}$ and T_{CO} in pure $CaFe_3O_5$ is small compared to those in other mixed-valent iron oxides.

The thermally proximate emergence of CO and CA phases and their spin orders between 289 and 320 K thus results from a remarkable coincidence of energy scales for the formation of two distinct electronic ground states and their long range spin orders in lightly doped $CaFe_3O_5$ samples. Both competing ground states are stabilized by delocalization of the minority spin t_{2g} electron between ferromagnetically aligned $t_{2g}^4 e_g^2$ Fe^{2+} ($S = 2$) and $t_{2g}^3 e_g^2$ Fe^{3+} ($S = 5/2$) spins, leading to trimeron units in the bc plane of the CO phase and ferromagnetic chains parallel to the a axis of the CA phase. The corresponding shortening of these Fe-Fe distances leads to lattice strains for the CO and CA phases that are effectively orthogonal, leading to rapid growth of large domains on cooling. Further studies could thus consider effects like sample crystallinity (single crystals compared to polycrystalline samples) which may also affect the phase separation.

VII. CONCLUSION

Temperature dependent powder neutron diffraction studies of $CaFe_{2.99}M_{0.01}O_5$ (M = Co, Mn) samples have revealed the sequence of electronic and magnetic phase transitions that occur in doped $CaFe_3O_5$ samples leading to electronic phase separation. Lattice strains resulting from intrinsic charge order (CO) in pure $CaFe_3O_5$ at $T_{CO} = 320$ K drive formation of a competing charge averaged (CA) phase that emerges at $T_{CA} = T_{CO}$ in these lightly doped samples. The CA phase emerges as magnetically ordered but the long range spin ordering transition is limited by domain growth and so occurs at a slightly lower temperature ($T_{CA(m)} = 301$ K for both samples). The spin ordering of the CO phase is not directly coupled to those of the other transitions, but is proximate in temperature with respective values of $T_{CO(m)} = 290(1)$ and $292(1)$ K for M = Co and Mn samples. The remarkable coincidence of energy scales for the formation of two distinct electronic ground states with differing lattice strains and their long range spin orders thus results in phase separation through a series of thermally proximate phase transitions in lightly doped $CaFe_3O_5$ samples.

The PND data and fitted models are available at [27].

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