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Long range electronic phase separation in $CaFe_3O_5$

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Incomplete transformations from ferromagnetic to charge ordered states in manganite perovskites lead to phase-separated microstructures showing colossal magnetoresistances. However, it is unclear whether electronic matter can show spontaneous separation into multiple phases distinct from the high temperature state. Here we show that paramagnetic $CaFe_3O_5$ undergoes separation into two phases with different electronic and spin orders below their joint magnetic transition at 302 K. One phase is charge, orbital and trimeron ordered similar to the ground state of magnetite, Fe_3O_4, while the other has Fe^{2+}/Fe^{3+} charge averaging. Lattice symmetry is unchanged but differing strains from the electronic orders probably drive the phase separation. Complex low symmetry materials like $CaFe_3O_5$ where charge can be redistributed between distinct cation sites offer possibilities for the generation and control of electronic phase separated nanostructures.

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Manganites such as $La_{0.7}Ca_{0.3}MnO_3$ and magnetite, Fe_3O_4, share similar physics as both have a spin-polarised conducting state near ambient temperature due to double exchange between ferromagnetically aligned Mn^{3+} and Mn^{4+} or Fe^{2+} and Fe^{3+} spins, respectively. Both undergo charge ordering on cooling, which for magnetite is accompanied by a lattice distortion below the much-studied Verwey transition at 125 K[1]. This was recently found to result from a complex ordering of Fe^{2+}/Fe^{3+} charge states, Fe^{2+} orbitals, and three-Fe trimeron groups[2]. However, long range phase segregation is observed below charge ordering transitions in many manganites[3-5] and related perovskites but has not been found in magnetite or related ferrite spinels.

Here, following recent studies of spin and charge ordering in non-spinel $MFe_{n-1}O_{n+1}$ ($n \geq 4$) ferrites with $M = Fe$[6,7], Mn[8,9] and Ca[10,11], we investigate $n = 4$ $CaFe_3O_5$ and discover long range electronic phase separation between a magnetite-like charge ordered phase and a charge averaged phase.

Results

Preparation and characterisation of $CaFe_3O_5$. $CaFe_3O_5$ was synthesised and characterised as described in Methods. The orthorhombic crystal structure consists of FeO_6 octahedra sharing edges to form infinite chains parallel to the a-axis and ribbons of three octahedra parallel to the bc-plane as shown in Fig. 1a. Magnetisation measurements (Fig. 1b) reveal a sharp magnetic ordering transition at $T_M = 302$ K and a small net magnetisation of 0.05 μ_B per $CaFe_3O_5$ unit with a moderate coercivity of 0.3 T at 2 K. Ceramic pellets of $CaFe_3O_5$ are semiconducting with a small magnetoresistance of −1% at 200 K (Fig. 1c), likely reflecting the small net magnetisation of the sample.

Evidence for electronic phase separation in $CaFe_3O_5$. A single high temperature (HT) crystalline phase of $CaFe_3O_5$ is observed above $T_M = 302$ K, but both powder synchrotron X-ray (Fig. 2a, b) and neutron diffraction data (Fig. 2c, d) reveal long range phase separation as diffraction peaks broaden or split into two components below the magnetic ordering transition as shown in Fig. 2a, c. The shift of the X-ray (002) peak to lower 2θ at 300 K evidences a small bulk lattice distortion due to spin ordering before separation into two phases at lower temperatures. Both low temperature phases have the same $Cmcm$ space group symmetry as the HT parent. Crystallographic results are shown in Supplementary Tables 1–5. Magnetic neutron diffraction peaks observed below T_M (Supplementary Fig. 1) show that one phase has magnetic propagation vector (½ 0 0) while the other has (0 0 0) (Fig. 2c), and a good fit to the data (Fig. 2d) was obtained using the magnetic structure models shown in Fig. 3. No additional broadening of magnetic peaks was observed showing that both magnetic orders have correlation lengths of at least ~200 nm. Both phases have collinear antiferromagnetic orders with moments parallel to the c-axis, but an important difference is that the (½ 0 0) phase has ferromagnetic (FM) alignment of spins within the three-atom ribbons parallel to the bc-plane, while the (0 0 0) has FM spin chains parallel to the a-axis. Although both orders are antiferromagnetic, the observation of a small net magnetisation below T_M suggests that one or both of the spin structures are canted. The fractions of the two phases are found to be different in the synchrotron and neutron diffraction experiments (Fig. 2a), consistent with a strain-driven phase separation being dependent on the thermal history of the sample.

Thermal evolution of lattice parameters from neutron and X-ray fits are, respectively, shown in Fig. 4a and Supplementary Fig. 2, and variations of internal structural quantities from both studies are shown in Fig. 4b–d to emphasise the reproducibility of
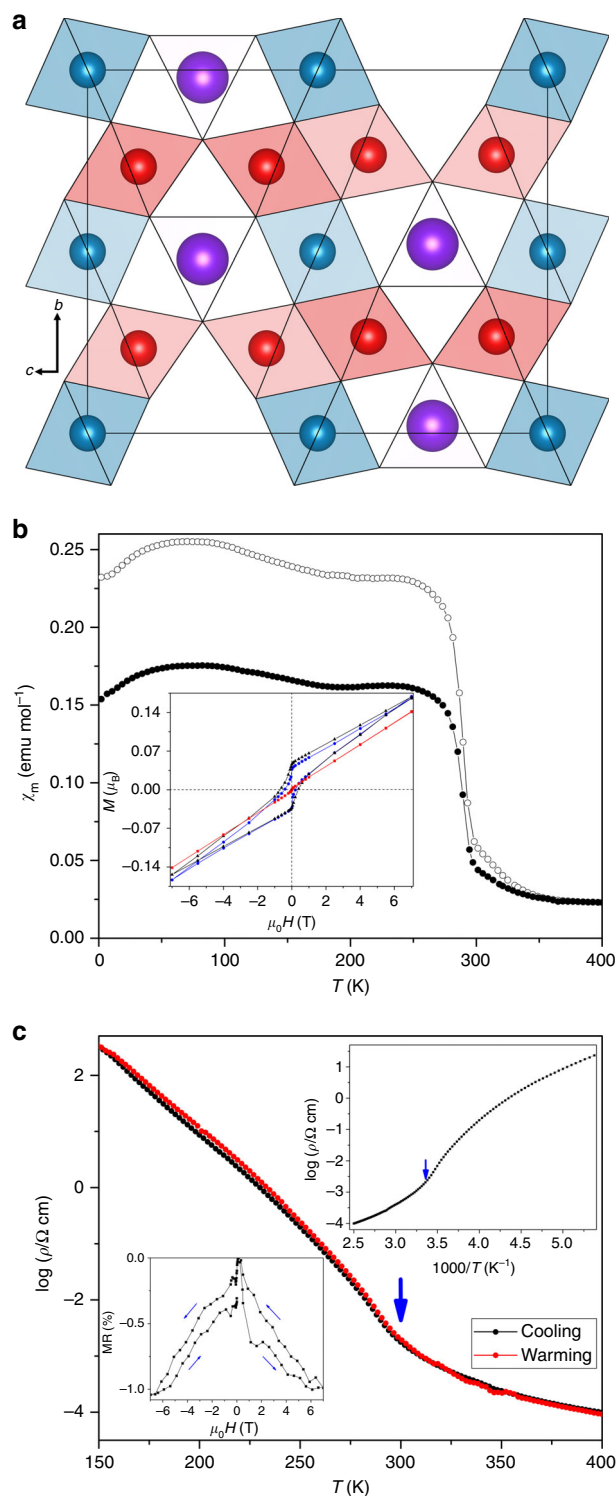
Fig. 1 Crystal structure and magnetisation studies of $CaFe_3O_5$. **a** Polyhedral projection of the $CaFe_3O_5$ structure showing FeO_6 octahedra in red/blue for symmetry inequivalent Fe1/Fe2 sites, and Ca within trigonal prismatic tunnels in purple. **b** ZFC (closed symbols) and FC (open symbols) magnetic susceptibilities for $CaFe_3O_5$, with insert showing magnetisation-field measurements at 2, 230 and 300 K (blue, black and red points respectively). **c** Log_{10} plot of the electrical resistivity of a sintered pellet of $CaFe_3O_5$ against temperature on cooling and warming, with the discontinuity at 302 K marked. Inset in the top right shows the plot against reciprocal temperature with a change in activation energy from 0.61 eV below T_M to 0.26 eV above the transition. Inset in lower left displays the magnetoresistance MR at 200 K

discovered structural differences between the two phases. Two inequivalent iron sites Fe1 and Fe2 are present in a 2:1 ratio in $CaFe_3O_5$, and in the HT phase they have respective Bond Valence Sums (BVSs) of 2.43 and 2.22, equivalent to formal charges of +2.75 and +2.50 when renormalized to the average of +2.67. Differing charge redistributions occur below the 302 K magnetic and phase segregation transition (Fig. 4b). In the phase with magnetic propagation vector (½ 0 0), the Fe1 and Fe2 BVSs diverge to very different values of 2.67(6) and 2.03(4) at 4 K, consistent with charge order (CO) of Fe^{3+} and Fe^{2+} respectively. The coexisting phase with (0 0 0) magnetic order shows the opposite behaviour as the Fe1 and Fe2 BVSs converge to similar values of 2.44(8) and 2.29(7) at 4 K showing that the electronic states at the two sites are not significantly different, hence this phase is charge averaged (CA).

Degenerate $3d^6$ Fe^{2+} states are subject to Jahn–Teller distortion which leads to tetragonal octahedral compression in magnetite[2], corresponding to negative values of the Q_{JT} distortion parameter. The Fe2 site in $CaFe_3O_5$ has a large negative Q_{JT} value due to intrinsic distortions within the HT structure (Fig. 4c), but below $T_M = 302$ K Q_{JT} becomes more negative for the CO phase, consistent with localisation of Fe^{2+} states, while the magnitude of Q_{JT} decreases in keeping with the observed increase in Fe2 site

valence for the CA phase. Jahn–Teller distortion at the Fe2 site in the CO phase leads to order of the t_{2g} orbital with minority spin electron density directed towards the two neighbouring Fe1 sites. Hence this localised orbital has the correct orientation to form a trimeron, a linear unit of three Fe ions formed by delocalisation of the minority spin electron in the ordered orbital of the central Fe^{2+} ion[2], as shown in Fig. 3c. Trimeron formation requires FM alignment of the three magnetic moments, Fe^{3+}–Fe^{2+}–Fe^{3+} CO, orbital order at the central Fe^{2+} in the plane of the three atoms, and shortening of the Fe–Fe distances within the trimeron[2]. All these conditions are observed in the Fe1–Fe2–Fe1 ribbons in the CO phase with shortening of Fe1–Fe2 distances below T_M observed in Fig. 4d, but none are fulfilled in the CA structure, so the observed spin orders and structural distortions in $CaFe_3O_5$ demonstrate that trimeron order is observed only in the CO phase. However, a slight shortening of Fe–Fe distances in the FM chains parallel to the a-axis is observed in the CA phase (Fig. 4d), consistent with a weak bonding effect from extended band states of the minority spin electrons. Fe1–Fe1 and Fe2–Fe2 distances are constrained to be equal (to a/2) and this is the likely driver for the observed averaging of charge states between the two sites in the CA phase so that their minority spin populations become more equal.
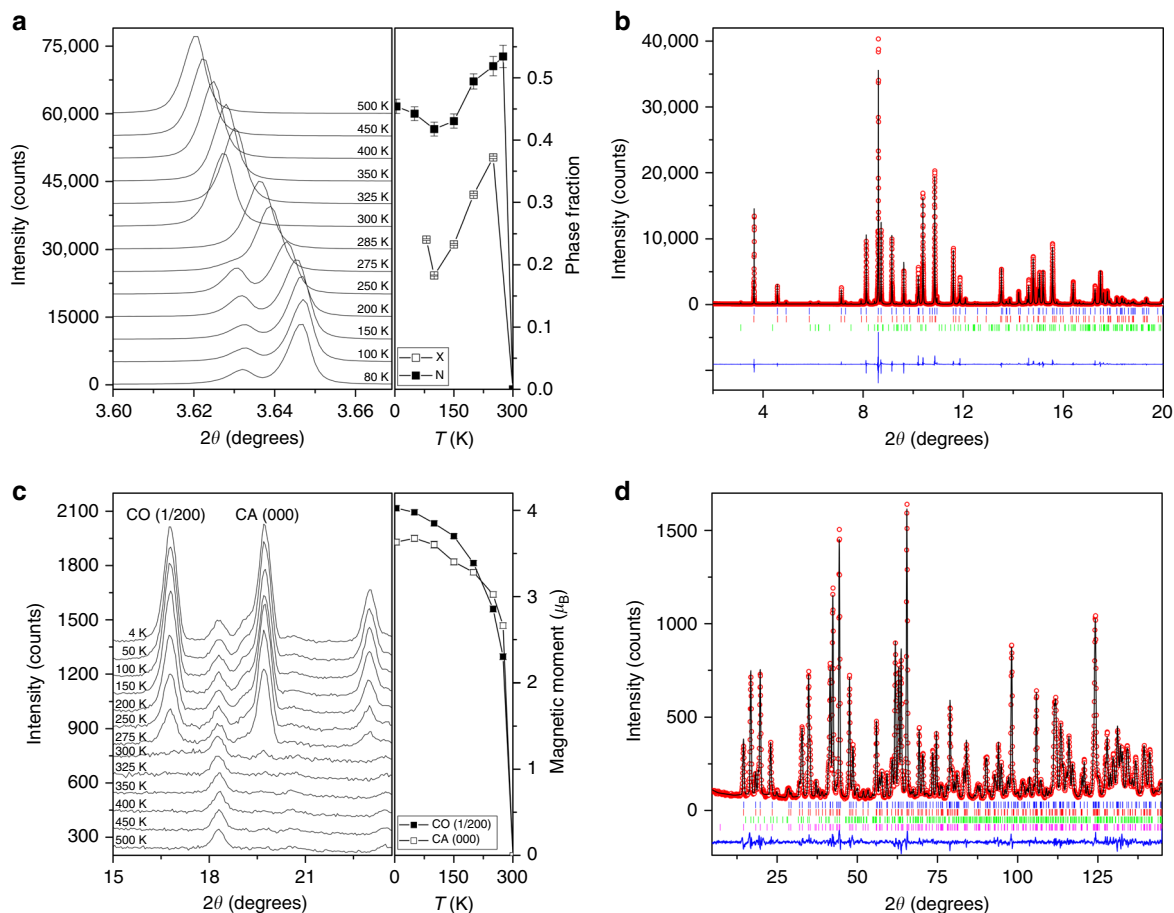
Fig. 2 Electronic phase separation of $CaFe_3O_5$. **a** Evolution of the X-ray (002) peak which shifts to lower 2θ when cooled to 300 K, just below the $T_M = 302$ K transition, with separation into two components at lower temperatures. The phase fractions of the charge averaged (CA) phase, obtained from synchrotron (X) and neutron (N) diffraction data are shown in the right-hand panel. Error bars are the estimated standard deviations calculated during profile fitting. **b** Rietveld fit to synchrotron powder diffraction profiles for $CaFe_3O_5$ at 80 K (R-factors $R_p = 9.35$ %, $R_{wp} = 11.0$ %), with blue and red tick marks indicating the two low temperature phases and green marks 2.3% of $Ca_2Fe_2O_5$ impurity. **c** The appearance of the magnetic reflections with propagation vectors of (000) for the CO phase and (½00) for the charge averaged (CA) phase below 302 K and the temperature evolution of their magnetic moments. **d** The Rietveld fit to neutron powder diffraction profiles for $CaFe_3O_5$ at 4 K (R-factors $R_p = 6.14$ %, $R_{wp} = 7.28$ %), with structural phases indicated with blue and red tick marks. The green and pink tick marks represent the magnetic phases with propagation vectors of (½00) and (000)
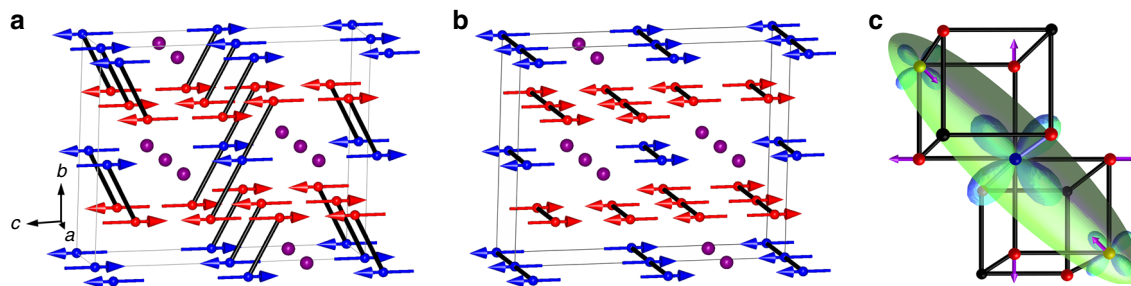
Fig. 3 Magnetic structures for the two phases of $CaFe_3O_5$. Fe1/Fe2 spins are shown in red/blue and Ca ions in purple. **a** Magnetic structure of the charge ordered (CO) phase $CaFe_3O_5$ with propagation vector (½ 0 0), with lines showing ferromagnetic order within trimerons. **b** Magnetic structure of the charge averaged (CA) phase, with (0 0 0) propagation and lines showing the ferromagnetic chain parallel to the x axis. **c** A trimeron unit as found in the CO structure (**a**) with bonding electron density represented as an ellipsoid. The size of the t_{2g} orbitals approximates the atomic populations. The atomic displacement arrows indicate the elongation of the four Fe–O bonds perpendicular to the Jahn–Teller contracted axis and the shortening of the cation–cation distances due to weak Fe–Fe bonding interactions
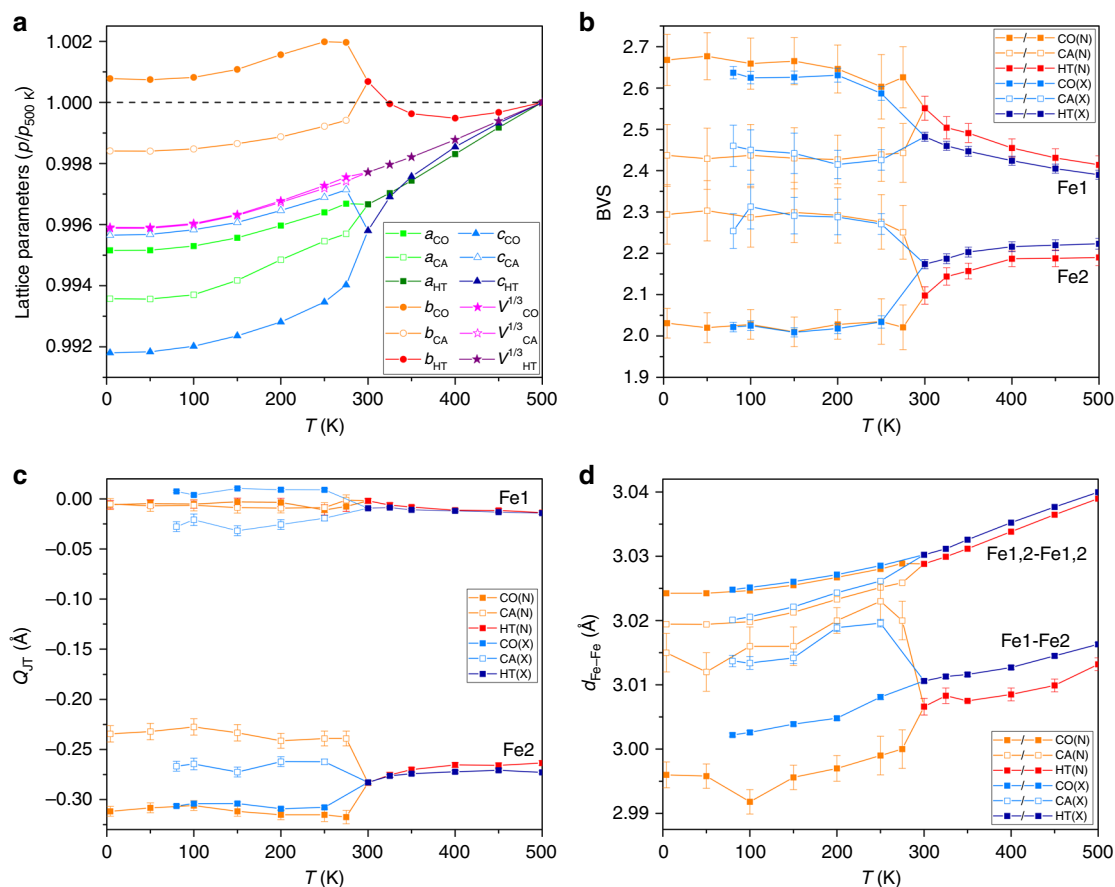
Fig. 4 Crystal structure parameters of $CaFe_3O_5$. **a** Changes in the lattice parameters relative to 500 K values obtained from PND ($a_{500 K} = 3.03896(1)$, $b_{500 K} = 10.01355(5)$ and $c_{500 K} = 12.67039(7)$ Å). Temperature dependence of the **b** BVS and **c** the amplitude of Jahn–Teller distortion (Q_{JT}) of the FeO_6 octahedra for the two sites in the high temperature (HT), charge ordered (CO) and charge averaged (CA) phases, obtained from neutron (N) and synchrotron X-ray (X) diffraction data. **d** The evolution of the Fe1-Fe2 bonding distance with temperature, with the lattice parameter (Fe1,2-Fe1,2) as reference. Error bars are the estimated standard deviations calculated during profile fitting

The electronic orders in the two phases of $CaFe_3O_5$ do not change the structural symmetry, but they lead to different cell distortions (Fig. 4a) as trimeron formation shortens the c-axis parameter in the CO phase, with a and b expanding to compensate, while the a-axis shortening in the CA phase leads to expansion of c. Although the overall cell volumes for the two components remain identical within error at low temperatures, the differing spontaneous strains from these lattice distortions are the likely driver for the long range separation as proposed for perovskite manganites[12–14]. Short range phase and strain fluctuations in the HT phase are evidenced indirectly below 350 K through divergence of zero field- and field- cooled susceptibilities in Fig. 1b, and changes in the slopes of b and c lattice parameters in Fig. 4a.

Charge ordering in one of the two low temperature phases is clearly a key driver for the long range electronic phase separation in $CaFe_3O_5$ and perovskite type oxides[15] although in $CaFe_3O_5$ this leads to the formation of orbital molecules[16], more complex

electronic objects than simple localised-charge ions. However, phase separation in $CaFe_3O_5$ occurs without a change of lattice symmetry in either component, demonstrating that strain variations within a given lattice are sufficient to drive long range segregation. Band structure calculations (shown in Supplementary Fig. 4 and Supplementary Table 6) confirm that these distortions are sufficient to stabilise CO in one structure but not the other for a realistic value of the Hubbard U-parameter. Phase separation in manganites usually results from an incomplete phase transition where a metallic HT FM phase is partially transformed to a charge ordered insulator, and the high and low temperature phases coexist to base temperature. A notable example is $Nd_{0.5}Sr_{0.5}MnO_3$ which on cooling was observed to order as a single FM phase at 250 K, then to phase separate into a mixture of FM and A-type antiferromagnetic (AFM-A) phases below 220 K, and finally to undergo a further phase separation into a mixture of FM, AFM-A and charge ordered AFM-CE phases below 150 K, with all three phases extant down to the lowest measured temperature of 15 K[17]. $CaFe_3O_5$ undergoes a genuine electronic phase separation in the sense that both of the two low temperature CA and CO phases are electronically and magnetically distinct from the HT paramagnetic state, and so is analogous to e.g. the separation of a fluid into a liquid and gas below a critical transition. Both low temperature $CaFe_3O_5$ phases are magnetically ordered and it is remarkable that they appear to share a common magnetic ordering temperature as shown in Fig. 2c although the spin-spin exchange interactions within the two magnetic structures will not be identical.

Another important difference is that phase separation in manganites is associated with substantial intrinsic disorder due to cation mixing, and a recent study has demonstrated that chemical ordering of cations in $(La_{1-y}Pr_y)_{1-x}Ca_xMnO_3$ suppresses long range phase separation[18]. $CaFe_3O_5$ is in principle a stoichiometric material although small strain variations due to the 4% substitution of Fe for Ca observed in our polycrystalline sample may tip the local balance between the energies of the two ground states leading to phase coexistence. The resulting disorder in magnetic interactions could also be important in stabilising the phase coexistence in a Griffiths-type model[19]. All Mn sites are electronically equivalent in the HT aristotype manganite perovskite structure but $CaFe_3O_5$ has a further electronic degree of freedom as charge can be redistributed between structurally inequivalent Fe1 and Fe2 sites, leading to the observed extremes of charge ordering (CO) in one phase and charge averaging (CA) in the other. This charge redistribution mechanism is akin to electronic separation models originally proposed for manganites[20,21], although couplings of both the charge redistribution degree of freedom and trimeron formation associated with charge and orbital ordering to the lattice appear to be important factors that drive phase segregation in $CaFe_3O_5$.

Discussion

In conclusion, the present study demonstrates that phase separation of a single HT paramagnetic state into two distinct low temperature phases with different long range spin and electronic orders occurs in $CaFe_3O_5$ when cooled below 302 K. Although both phases are antiferromagnetic overall, the formation of different FM units within them is coupled to the electronic orders; one phase has full Fe^{2+}/Fe^{3+} CO associated with trimeron formation, but CA stabilises FM chains in the other phase. Weak Fe–Fe bonding driven by the FM orders introduces different lattice strains into the two phases although no change of structural symmetry occurs, and strain variations within the polycrystalline sample tip the local balance between the energies of the two phases leading to phase coexistence. $CaFe_3O_5$ thus links the trimeron-ordering of magnetite

to the microstructural physics of perovskite manganites. $CaFe_3O_5$ also demonstrates new possibilities for more complex 'electronically soft matter'[22] than in perovskites where orbital molecule formation and redistribution of charge between distinct cation sites offer additional degrees of freedom for generation and potential control of electronic phase-segregated nanostructures.

Methods

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Author contributions

K.H.H. and J.P.A. designed the concept for this study. K.H.H., A.M.A.-L., and C.R. performed the experimental work and data analysis, and J.C. performed the band structure calculations. K.H.H. and J.P.A. wrote the manuscript with inputs from all authors.

Additional information

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