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Temperature driven self-doping in magnetite

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Abstract

Magnetite is one of the most fascinating materials exhibiting the enigmatic first-order Verwey transition which is conventionally manipulated through chemical doping. Here we show that heating magnetite results in a spontaneous charge reordering and consequently a hole self-doping effect at the octahedral sublattice. Core level x-ray spectroscopy measurements combined with theory uncovers that there are three regimes of self-doping that map the temperature dependence of the electrical conductivity and magnetism up to the Curie temperature. Our results provide an elegant analogy between the effect of chemical doping and temperature-driven self-doping on trimerons in magnetite.

21 Magnetite (Fe_3O_4) is one of the most abundant iron bearing minerals on earth and finds
22 many applications in areas such as palaeomagnetism [1–3], medicine [4], data recording [5]
23 and ultrafast magnetic sensors [6, 7] among others [8]. It is the first example for an oxide to
24 show a metal to insulator transition (the Verwey transition at $T_V \approx 123\text{ K}$ [9]). Fe_3O_4 has
25 a cubic inverse spinel structure above T_V with Fe^{2+} occupying octahedral interstitial sites
26 (B-sites) while Fe^{3+} are equally distributed over the octahedral and tetrahedral interstitial
27 sites (A-sites) [10]. The cubic structure of Fe_3O_4 distorts to a monoclinic superstructure (Cc
28 space group symmetry) below T_V forming a complex network of linear orbital molecules
29 composed of three Fe B-site units called trimerons [11].

30 Short-range structural fluctuations linked to the presence of trimerons were reported
31 to exist up to the Curie temperature using interatomic pair distribution function derived
32 from total x-ray scattering data [12], diffuse scattering [13] and resonant inelastic x-ray
33 scattering [14, 15]. These structural fluctuations emerge from the magnetic ordering and are
34 regarded as the primary electronic instability at the origin of the Verwey transition [12, 16].
35 Unveiling the mechanism behind the collapse of structural correlations in magnetite and
36 the temperature evolution of trimerons would significantly shape our understanding of the
37 Verwey transition.

38 We performed Fe K_{α_1} high-energy resolved fluorescence-detected x-ray absorption spec-
39 troscopy (HERFD-XAS) measurements at ID26 of the European Synchrotron Radiation
40 Facility [17, 18] (Fig. 1(a)) as a function of temperature on a stoichiometric single crystal of
41 Fe_3O_4 (Fig. S8 and S9). HERFD-XAS spectra are measured with a fluorescence detector
42 such that the life time broadening of the $1s$ core hole no longer appears in the spectra [19].
43 Two regions of the spectrum can be identified: (i) the K pre-edge from 7110 eV to 7120 eV,
44 and (ii) the K main-edge from 7120 eV to 7200 eV shown in Fig. S1. The spectral shape
45 and the intensity of the K pre-edge is sensitive to the local site symmetry while the K
46 main-edge energy position is indicative of the average oxidation state of all absorbing ions
47 [20, 21]. We found that the main edge position remains almost constant indicating that the
48 overall oxidation state is preserved (Fig. S5 and S6), however spectral changes are observed
49 in the K pre-edge region in Fig. 1(a). The intensity of the K pre-edge is redistributed at
50 higher temperatures in a manner which cannot be accounted for by a Boltzmann population
51 of excited states or phonons (see supplementary). The intensity of the K pre-edge peak
52 asymmetrically broadens towards lower energies suggesting a reordering of the Fe charges.

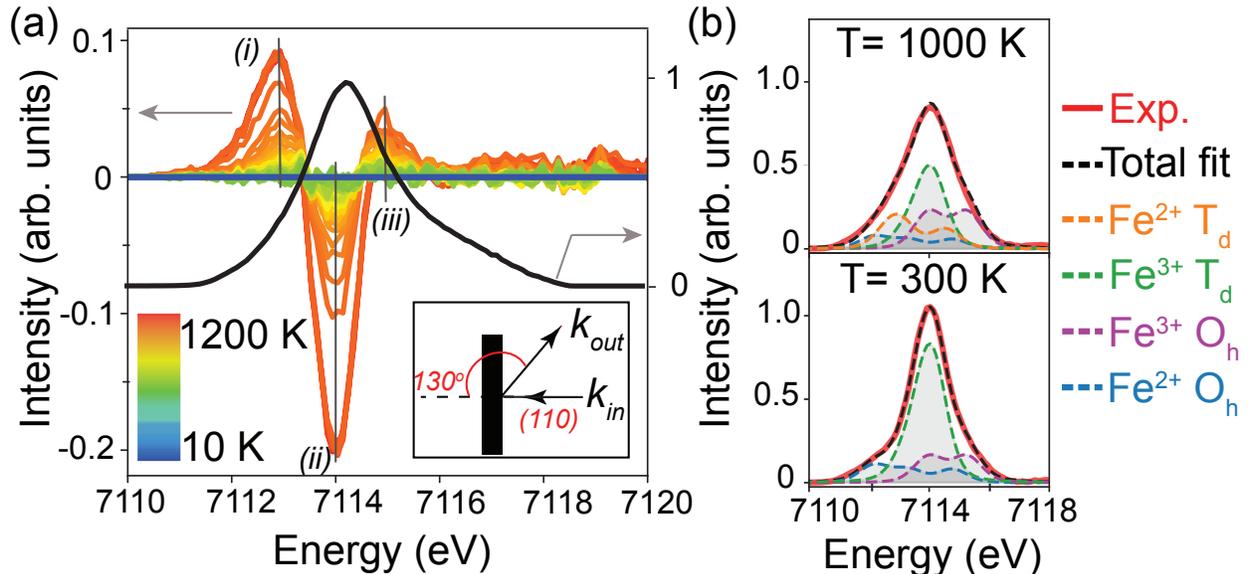


FIG. 1. Fe K_{α_1} HERFD-XAS in Fe_3O_4 measured from 10 K to 1200 K. (a) An exemplary Fe K pre-edge measurement at $T = 300$ K and the difference signal of the Fe K pre-edge as a function of temperature referred to the lowest measurement at $T = 10$ K. A sketch of the scattering geometry is shown in the inset. (b) The K pre-edge at $T = 300$ K (bottom) and $T = 1000$ K (top) together with theoretical simulations using a ligand field multiplet model (dashed lines) illustrating the contributions of the various Fe sites to the spectrum. T_d and O_h stand for tetrahedral and octahedral sites respectively.

53 The K pre-edge is a powerful tool to study the charge redistribution among octahedral
 54 and tetrahedral sites as it acts as a "magnifying glass" (with a magnification of about $4\times$
 55 as determined from our previous work using K pre-edge XMCD and XMLD [22]) directed
 56 towards tetrahedral sites. The K pre-edge is formally attributed to quadrupole transitions
 57 from the $1s$ electrons to the empty $3d$ orbitals (in many-body language, quadrupole transi-
 58 tions between the $1s^23d^n \rightarrow 1s^13d^{n+1}$ configurations). This is indeed the case for octahedral
 59 sites giving rise to a weak K pre-edge intensity. The situation is different for tetrahedral
 60 sites because they lack centrosymmetry which allows for $3d$ - $4p$ orbital mixing [23]. Conse-
 61 quently, the K pre-edge gains intensity from both electric quadrupole and partially allowed
 62 dipole transitions leading to an intense K pre-edge. Any change in the tetrahedral sites is
 63 enhanced which allows us to effectively quantify charge reordering between the two sites.

64 The contributions of the three Fe sites to the K pre-edge of Fe_3O_4 at room temperature

65 are shown in Fig.1(b) using ligand field multiplet calculations [24–27]. The main intensity
66 of the K pre-edge arises from the tetrahedral sites (plotted in green) despite the fact that
67 only $\frac{1}{3}$ of the Fe sites reside in tetrahedral sites while $\frac{2}{3}$ reside in octahedral sites (plotted
68 in purple and blue). Theoretical simulations show that the intensity redistribution of the
69 K pre-edge of Fe_3O_4 at 1000 K is a result of a charge redistribution between octahedral and
70 tetrahedral sites. The contribution of Fe^{3+} in tetrahedral sites (green) decreases and a new
71 contribution related to the presence of Fe^{2+} in tetrahedral sites (orange) rises. We note that
72 the proposition that Fe reorders in Fe_3O_4 at higher temperatures was previously suggested
73 based on thermopower measurements [28], neutron powder diffraction [29] and Mössbauer
74 spectroscopy [30, 31]. A concrete analysis of the redistribution has been so far lacking
75 because deducing the cation occupation from macroscopic thermopower measurements de-
76 pends on the details of the model used while extensive neutron scattering measurements
77 combined with bond valence sum estimates are missing. Although Mössbauer spectroscopy
78 provides this information, there are some inconsistencies in quantification between studies
79 possibly related to the qualities of crystals used.

80 We quantified the site occupation of Fe^{3+} and Fe^{2+} ions in octahedral and tetrahedral
81 interstitial sites using ligand field multiplet calculations as a function of temperature (see
82 Fig.2 and Fig. S4 showing an exemplary fit). A clear trend is observed: Fe^{2+} progressively
83 decreases in octahedral and increases in tetrahedral sites as the temperature is increased.
84 A counter effect also takes place where Fe^{3+} decreases in tetrahedral sites and increases in
85 octahedral interstitial sites. This redistribution can be parametrised using two variables, α
86 and β , as described by Eqn. 1.

$$\alpha Fe_{O_h}^{2+} + \beta Fe_{T_d}^{3+} + (8 - \alpha) Fe_{T_d}^{2+} + (16 - \beta) Fe_{O_h}^{3+} \quad (1)$$

87 The parameters $\alpha = \beta = 8$ describe an inverse spinel structure. On the other extreme,
88 $\alpha = \beta = 0$ describe a normal spinel structure. Intermediate structures are also possible
89 with $\alpha \neq \beta$. The total number of Fe and charge stays conserved, however, the total number
90 of Fe in the octahedral and tetrahedral interstitial sites changes for $\alpha \neq \beta$. The evolution
91 of the α and β parameters as a function of temperature is shown in Fig. 3(a). We can
92 identify three main regimes based on the behaviour of the α and β parameters as a function
93 of temperature:

94 1. $T \leq 330$ K: The local charge distribution is preserved over this temperature range and

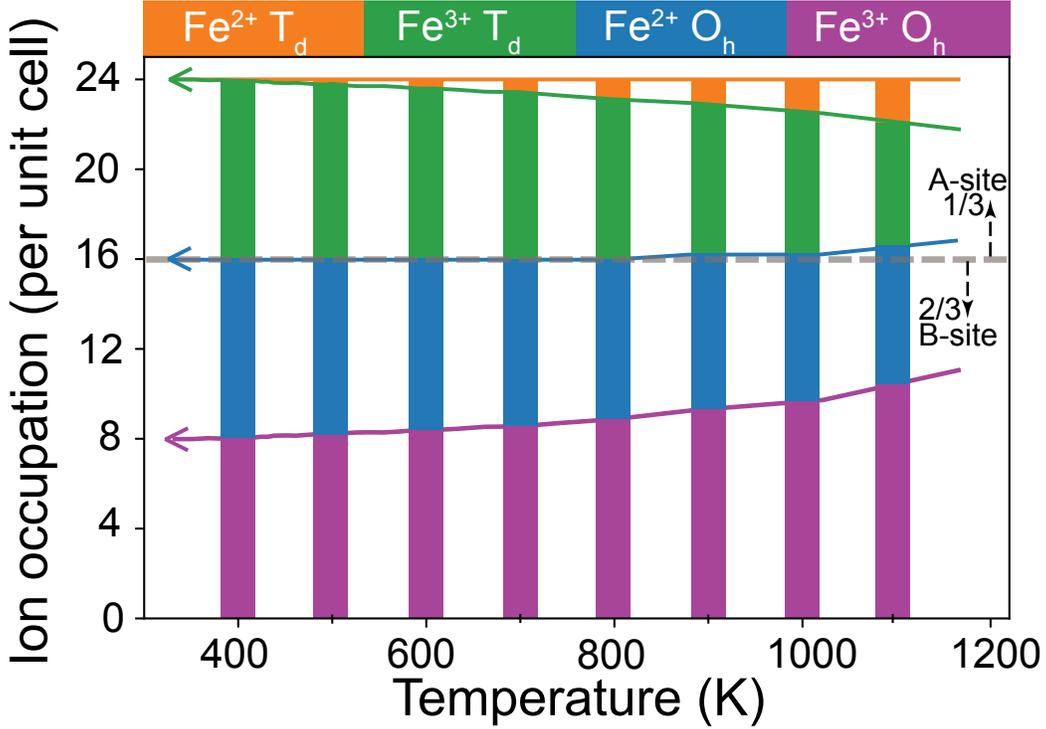


FIG. 2. Occupation of Fe³⁺ and Fe²⁺ ions in octahedral (O_h , plotted in purple and blue) and in tetrahedral (T_d , plotted in green and orange) sites per unit cell of Fe₃O₄ shown for the temperatures between 300 K-1200 K where we observe charge redistribution. The vertical bars are shown to guide the eye. Note that the total Fe charge remains constant (see text).

resembles that of the low temperature phase.

2. $330 \text{ K} \leq T \leq 840 \text{ K}$: The charge redistributes between the octahedral and tetrahedral sites in this temperature range. This regime is identified by an initial linear subrange to 500 K followed by a significant exponential temperature dependence with $\alpha = \beta$. A full charge is exchanged between the octahedral and tetrahedral sublattices at $T = 840 \text{ K}$ where the unit cell becomes: $[Fe_1^{2+}, Fe_7^{3+}]_{T_d}[Fe_7^{2+}, Fe_9^{3+}]_{O_h}O_{32}$.
3. $T \geq 840 \text{ K}$: The onset of the last regime is identified by a deviation from the equality between α and β . This implies that cations are exchanged between the two sublattices where Frenkel-type point defects are formed [32] and the occupation of the interstitial B sites increases ($\alpha > \beta$). At the highest temperature of our measurement, we find that the unit cell becomes: $[Fe_2^{2+}, Fe_5^{3+}]_{T_d}[Fe_6^{2+}, Fe_{11}^{3+}]_{O_h}O_{32}$.

We performed principle component analysis (PCA) to mathematically confirm the need

107 of two independent parameters (linear combinations of α and β) to explain the variation in
 108 our data across the full temperature range [33]. Fig. S12 shows the PCA results where two
 109 principle components are required to explain the experimental data and carry accumulatively
 110 99.95% of the variance. To our knowledge, this is the first work revealing the existence of
 111 this intermediate charge distribution intertwined with point defects in stoichiometric Fe_3O_4 .
 112 These defects behave as an ideal solute according to the extended work of Diekmann and
 113 coworkers on oxygen activity in Fe_3O_4 [32, 34–38]. This is also inline with reported kinetics of
 114 diffusion in doped ferrites that show that interlattice diffusion processes become relevant for
 115 $T \sim 500^\circ\text{C}$ [39]. Results from neutron and x-ray diffraction report an anomalous expansion
 116 in the dimensions of the tetrahedral polyhedrons above the T_C , while the expansion of the
 117 octahedral polyhedrons remains monotonous [29, 40]. A possible explanation could be due
 118 to the significant increase of $[\frac{Fe^{2+}}{Fe^{3+}}]_A$ (with $\alpha > \beta$) and taking into account the larger radius
 119 of Fe^{2+} with respect to Fe^{3+} cations (see Fig. S11). However, this remains to be validated
 120 with rigorous refinement of diffraction experiments above T_C .

121 The three charge ordering regimes match the evolution of key physical properties of Fe_3O_4
 122 exquisitely well. For example, the temperature dependence of the electrical conductivity of
 123 Fe_3O_4 maps on to the three regimes as can be seen in Fig. 3(b). The electrical conductivity
 124 increases from T_V to about 330 K ($\alpha = \beta = 8$) exhibiting a semi-conductor-like behaviour.
 125 This is then followed by regime II where the charge ordering parameters begin to decrease
 126 and is marked by a decrease in the conductivity with temperature as typical for metal-
 127 like behaviour. A saddle point is seen as a minimum in the derivative signal in Fig. S10
 128 corresponding to $T = 500$ K which corresponds to the end of a linear subrange of regime II.
 129 Finally, a modest rise of the conductivity with temperature is observed marking the onset
 130 of the third regime at temperatures above 840 K.

131 A useful way to think about the temperature dependent evolution of the $[\frac{Fe^{2+}}{Fe^{3+}}]_B$ is in
 132 terms of B-site hole self-doping in analogy to the widely studied chemical doping of Fe_3O_4
 133 [41, 42]. This is because one expects to find analogies at critical doping levels given that the
 134 fundamental building block of the low temperature charge-ordered structure, the three-site
 135 linear magnetic polaron referred to as trimeron, persists beyond T_V and up to T_C as seen
 136 in Fig. S10(c) [12]. It is possible to evidence the multi-site trimerons in Fe_3O_4 using XAS
 137 through the accompanying local Jahn-Teller distortion at the central Fe^{2+} ion, however, our
 138 data cannot provide information about the lattice distribution of trimerons.

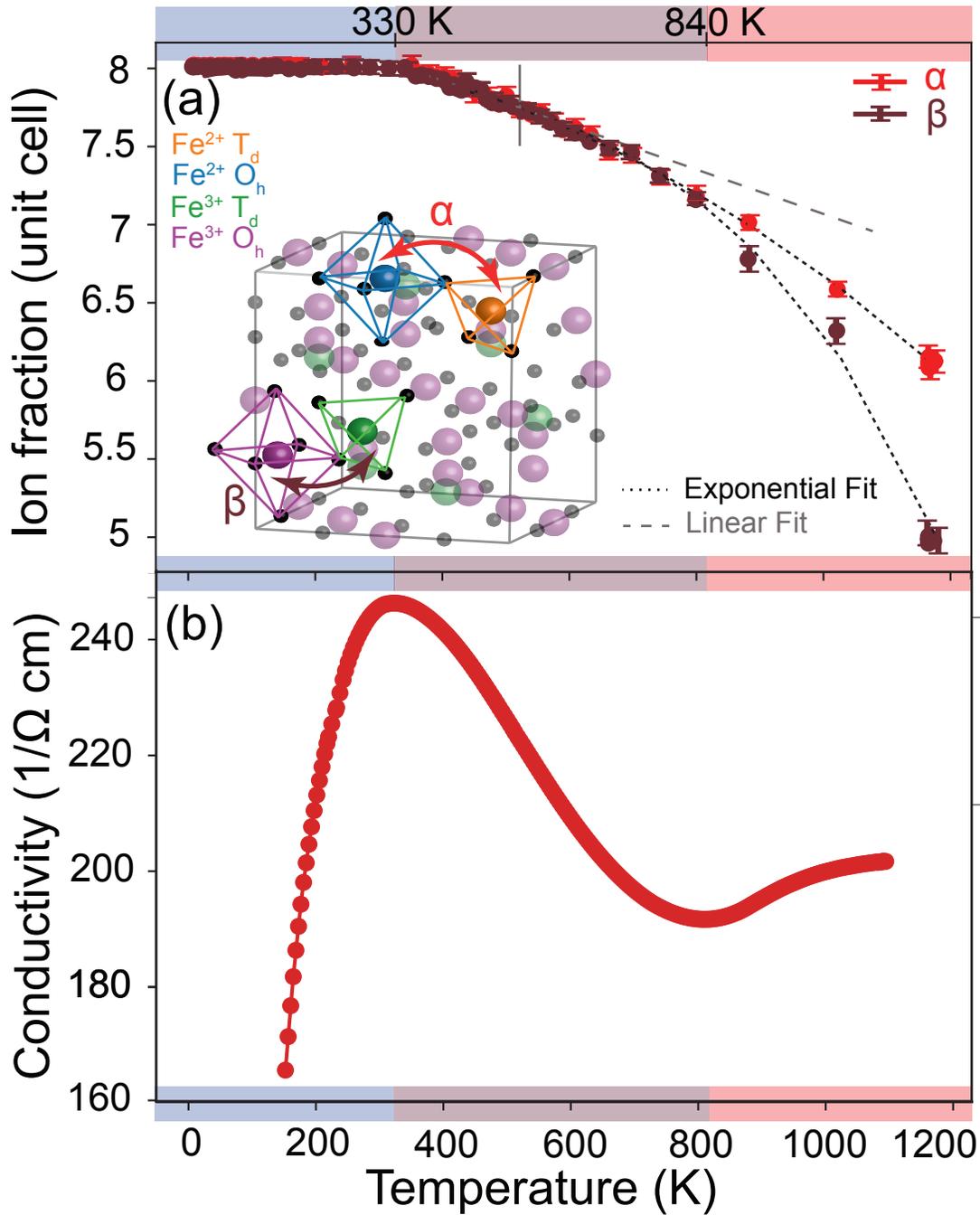


FIG. 3. (a) Temperature evolution of the redistribution parameters α (red) and β (brown) in Fe_3O_4 . Linear and exponential fits are plotted in dashed gray and black dashed lines. A cartoon of the ion transfer in a unit cell of Fe_3O_4 is shown in the inset. (b) Temperature dependence of the electrical conductivity of Fe_3O_4 . The colour code on the x-axis of the figure illustrates the regimes described in the text.

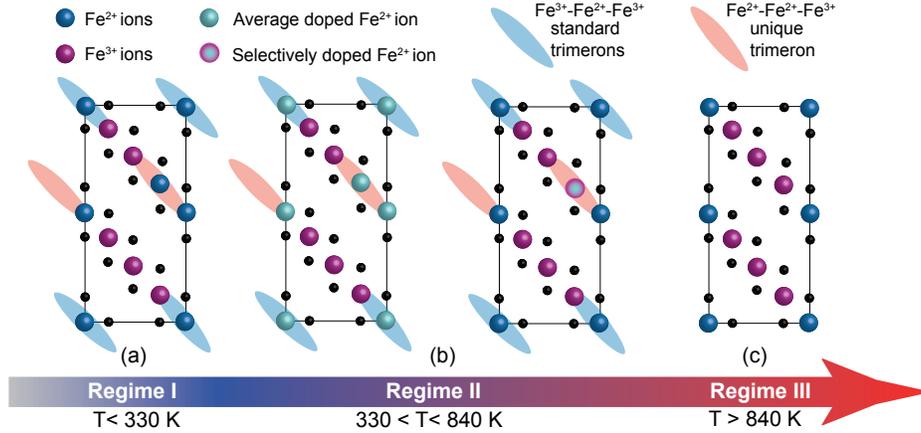


FIG. 4. Proposed possible model for the effect of temperature on Fe_3O_4 . The Cc supercell is shown with the (100) surface of cubic magnetite showing trimers (shadowed) in the surface layer. Only the B-sites are shown where the Fe^{2+} -like and Fe^{3+} -like ions are plotted in blue and purple respectively. Oxygen is shown in black. The B42 like-site is shown encompassed with a red trimeron. (a) In regime I, local correlations in Fe_3O_4 resemble that of the low temperature phase. (b) Self-doping occurs in regime II where initially the entire unit cell mitigates the hole and depicted in light blue. At the self-doping $\delta = 0.023$, the hole localizes on a single trimeron. (d) Increasing the self-doping level beyond a critical level where the Fe^{2+} B42 like-site fully oxidizes to Fe^{3+} leads to the collapse of all local correlations. We emphasize that the current illustration represents a proposed snapshot in time of structural fluctuations.

139 In this work we propose an elegant analogy between the temperature-driven self-doping at
 140 the B-sublattice far above the Verwey temperature and the chemical doping effect observed
 141 at low temperature (Fig. 4). We propose that the changeover from the linear temperature
 142 dependence of the charge ordering is triggered by a critical hole self-doping level of 0.023
 143 (reached at $T=500$ K as seen in Fig. S10) similar to the effect of doping on the Verwey
 144 transition [43]. Essentially before this level of doping, the short-range trimeron are not
 145 significantly perturbed and we suspect that the partial hole doped into the B sublattice is
 146 mitigated by the entire dynamical network. As the self-doping level increases above ~ 0.023 ,
 147 Fe_3O_4 transitions to a selective self-doping on one precise trimeron. We emphasize that at
 148 these temperatures trimers are not static, however, per snapshot, the self-doped hole
 149 resides on one trimeron selectively as evidenced by the local Jahn-Teller distortion observed
 150 by XAS. The selective self-doping progresses until the Fe^{2+} cation is fully oxidised to Fe^{3+}

151 (i.e. B-site $\text{Fe}^{3+}:\text{Fe}^{2+} = 9 : 7$ as seen in Fig. 3). This considerable perturbation is of a critical
152 consequence: the trimerons completely breakdown. The signature of this is imprinted on
153 the collapse of magnetism (Fig. S9 [44]) and the changeover of the electrical conductivity
154 (Fig.3(b)).

155 In summary, this work demonstrates that a charge reordering occurs in Fe_3O_4 from 330 K
156 leading to a contineous and reversible hole self-doping effect at the B-sublattice. Despite
157 its simplicity, our model captures the prominent features of our experimental data and
158 suggests that α and β are adequate descriptors for correlations in Fe_3O_4 . Temperature
159 driven self-doping provides a unique adjustable experimental handle intimately connected
160 to chemical doping. Beyond these results, we envision using the combination of K pre-
161 edge HERFD-XAS and theoretical calculations to solve open questions in palaeomagnetism
162 where understanding correlations in iron minerals under high pressure and temperatures is
163 essential.

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