Ultrafast generation of hidden phases via energy-tuned electronic photoexcitation in magnetite

B. Truc1,2, P. Usai1, F. Pennacchio2, G. Berruto3, R. Claude2, I. Madan4, V. Sala5, T. LaGrange6, G. M. Vanacore6,7, S. Benhabib4,8, and F. Carbone4,9

Affiliations are included on p. 6.

Edited by Angel Rubio, Max-Planck-Institut für Struktur und Dynamik der Materie, Hamburg, Germany; received October 16, 2023; accepted April 26, 2024

Phase transitions occurring in nonequilibrium conditions can evolve through high-energy intermediate states inaccessible via equilibrium adiabatic conditions. Because of the subtle nature of such hidden phases, their direct observation is extremely challenging and requires simultaneous visualization of matter at subpicosecond and submicrometer scales. Here, we show that a magnetite crystal in the vicinity of its metal-to-insulator transition evolves through different hidden states when controlled via energy-tuned ultrashort laser pulses. By directly monitoring magnetite’s crystal structure with ultrafast electron diffraction, we found that upon near-infrared (800 nm) excitation, the trimeron charge/orbital ordering pattern is destroyed in favor of a phase-separated state made of cubic-metallic and monoclinic-insulating regions. On the contrary, visible light (400 nm) activates a photodoping charge transfer process that further promotes the long-range order of the trimerons by stabilizing the charge density wave fluctuations, leading to the reinforcement of the monoclinic insulating phase. Our results demonstrate that magnetite’s structure can evolve through completely different metastable hidden phases that can be reached long after the initial excitation has relaxed, breaking ground for a protocol to control emergent properties of matter.

metal-to-insulator transition | ultrafast electron diffraction | magnetite | Verwey transition | light-induced phenomena

At equilibrium, phase transitions follow an adiabatic pathway within the material free-energy landscape, and the transition is characterized by a succession of thermodynamic equilibrium states between two global minima. Instead, using ultrashort laser pulses drives the transition out-of-equilibrium and induces a distinct pathway by transiently changing the coupling between the relevant degrees of freedom. Light-driven phase transitions reveal the presence of hidden phases of matter (1–9). Such hidden phases are not only of interest from a fundamental point of view but also bear potential for ultrafast technological devices (9, 10). Magnetite (Fe₃O₄) exhibits a complex interplay between the crystal structure (11), charge (12–15) and orbital orders (16, 17), which leads to the emergence of a metal-insulator transition (MIT) in the vicinity of 125 K, known as the Verwey transition (VT) (18). It is found that the structural changes play a key role in VT (19, 20). Above Verwey temperature (Tᵥ), magnetite has a cubic inverse spinel Fd₃m structure formally written Fe³⁺[Fe²⁺Fe³⁺]O₄, the first Fe³⁺ (A-type) occupied the tetrahedral sites, whereas the [Fe²⁺Fe³⁺] (B-type) occupied the octahedral sites. Below the Tᵥ, the symmetry changes from the cubic Fd₃m to the monoclinic Cc phase (11). In the low-temperature (LT) phase, a new kind of bond dimerized state, the so-called trimeron, has been observed and shown to form a long-range order (21, 22). The trimeron unit results from multiple cooperative effects, including charge, t₂g orbital orderings, and strong electron–phonon coupling (23). Therefore, trimerons are deemed to be the key actor of VT, which has been recently described microscopically as an order–disorder transition from a fluctuating trimeron network to a commensurate long-range order below Tᵥ (24–26). Optical experiments have shown that light offers the intriguing possibility to manipulate such charge fluctuations resulting in tuning the electron–phonon coupling (26) and suggesting that the light-induced transition can be very orbital-selective. Here, we directly visualize the out-of-equilibrium structural dynamics of magnetite employing ultrafast electron diffraction (UED). We tracked the lattice evolution of magnetite across the photoinduced MIT. We show that, depending on the photon energy of the femtosecond pulses used in the experiment, we trigger different electronic excitations, consequently leading to distinct nonequilibrium metastable structural states.
1. Results

We first monitored the quasi-adiabatic transition in magnetite. We investigate the structural changes by decreasing the temperature from 150 K down to 40 K and simultaneously following the quasi-static change of the diffraction pattern along the [110] direction where anomalies attributed to the trimers have been recently observed (27). In Fig. 1 A and B, we show the static diffraction patterns of magnetite measured above and below \( T_V \), respectively. Specifically, we monitor the changes of the \((6\,6\,0)\) Bragg peak of the cubic phase which transforms to \((12\,0\,0)\) in the monoclinic phase (SI Appendix). The subscripts \( c \) and \( m \) denote the cubic and monoclinic phases, respectively. We observe a significant modification of the peak position from which we extract the atomic interplanar expansion or compression shown in Fig. 1 F. This is accompanied by a drop in the diffraction intensity as illustrated in Fig. 1 G. Such intensity drop results from the combination of two concomitant factors: i) the lowering of the structure factor when transitioning from a high-symmetry cubic phase to a lower symmetry monoclinic structure and ii) the incoherent electron scattering process through multiple microsized structural domains (twins) that emerge in LT phase (28). Both factors generate additional reflections. However, due to their expected weaker intensity, no additional peak was identified in our data (SI Appendix). Across VT, at 117 K, the cubic lattice transforms into the monoclinic phase, which is evidenced by the expansion of the lattice along the \([1\bar{1}0]\) direction, as sketched in Fig. 1 D. This specific expansion significantly changes the shear strain \( \varepsilon_{xy} \). In addition, it causes a significant softening in the shear elastic constant \( c_{44} \), as reported in ultrasound measurements (29). Although our technique is moderately surface sensitive (\( \sim 5 \) nm), the agreement between the monitored position shift of the Bragg peak from our data and the reported softening in the elastic constant \( c_{44} \) demonstrates that our observations are representative of bulk dynamics.

We retrieved the symmetry of the order parameter (OP) \( \Delta \) across VT based on the framework of Ginzburg–Landau and a fundamental group theory analysis (30). We ascribed the measured shear strain \( (\varepsilon_{xy}) \) being strongly coupled to \( \Delta \), and therefore \( \Delta \) admits a \( T_{2g} \) symmetry with one nonzero component, i.e., \( \Delta = (\Delta_{xy}, 0, 0) \) (SI Appendix).

Using detailed group theory calculations, several authors have identified the set of phonons, including \( \Delta_5, X_3, \) and \( \Gamma^{+5} (T_{2g}) \), as the structural OPs (31–33). Furthermore, ab initio calculations have demonstrated the strong coupling between these structural OPs and the \( T_{2g} \) orbital ordering within a trimeron (31). Therefore, we conclude that the trimeron arrangement along...
the [110] direction is a conceivable OP candidate with T$_{2g}$
representation. The OP with T$_{2g}$
representation was suggested recently by electron diffraction measurements, where the authors consider an anomalous electronic nematic phase above T$_v$ with a T$_{2g}$
representation which involves a different set of rotational symmetry breaking than the usual ones (34).

Having discussed the equilibrium phase transition, we now investigate the structural dynamics of the nonadiabatic MIT in magnetite—initially kept at 80 K—by tracking the (T2 0 0)$_m$
Bragg reflection response following the ultrafast photoexcitation. We used two different wavelengths, 800 nm and 400 nm at 2.9 mJ/cm$^2$ and 1.2 mJ/cm$^2$ incident fluence, respectively. The fluence used for 800 nm corresponds to the intermediate fluence regime (35).

Fig. 2A shows the structural dynamics following 800 nm photoexcitation. The (T2 0 0)$_m$
atomic planes undergo a maximum compression of around $-0.06\%$. Based on our static data shown above (Fig. 1), the compression of the monoclinic lattice along the [110] direction denotes the transformation toward a cubic structure, consistent with ref. 35. Their recent out-of-equilibrium optical measurements have shown a photoinduced phase separation between insulating regions and metallic islands at LT through 800 nm laser pulses in a similar fluence regime. This observation is supported by pump–probe X-ray diffraction measurements (36), where the authors attribute the insulating state to the monoclinic regions and the metallic state to the cubic islands. Expanding the investigation range of previous measurements that were limited to the first 10 ps (34–36), our data unveil the complex establishment of the hidden phase which lasts approximately 50 ps and interestingly follows three compression stages. First, during the first 22 ps (N$^0$1), an abrupt compression of $-0.03\%$ occurs. In the second stage (N$^0$2) between 22 and 27 ps, the lattice undergoes a minor contraction. Finally, the third step (N$^0$3) emerges and adds an extra $-0.03\%$ to the lattice compression. This multistep process is characteristic of the presence of distinct dynamic processes, such as electron–phonon coupling and phonon–phonon interaction (34, 37). Note that the electron–electron interaction is expected to occur on a faster timescale <300 fs (36), beyond the temporal resolution in these experiments. The relaxation process also evolves with multiple timescales. Qualitatively, the first recovery stage (N$^0$4) occurs from 50 ps to 126 ps and reaches an intermediate compressed state close to $-0.03\%$, which interestingly corresponds to the value of the process N$^0$3. Then, a second long process occurs toward the total recovery (N$^0$5) to the equilibrium phase, which is still not reached after 1.3 ns (SI Appendix). In a second dataset with a slightly higher fluence (SI Appendix), we confirm the multiple compression stage process and show that each stage’s duration and amplitude depend on the fluence used.

In Fig. 2C, the response of the Bragg peak intensity after the 800 nm photoexcitation shows a drop. Taking only into account the recovery toward the higher symmetry cubic high temperature phase after the 800 nm photoexcitation, we expect an increase in the intensity, which we do not observe. This observation

![Fig. 2. Evolution of the lattice change compression/expansion along the [110] direction (A) under 800 nm and (B) 400 nm photoexcitation. In (A), the shaded areas show multiple compression stages. Normalized intensity evolution under (C) 800 nm and (D) 400 nm photoexcitation. The time constants extracted from an exponential fit (SI Appendix) are 16.0 ± 5.0 ps, 10.7 ± 1.5 ps, 20.1 ± 4.2 ps for the stage 1, 3, and 4, respectively, in (A) and 13.3 ± 2.0 ps in (B). Solid lines are guides to the eye. The error bar represents the SD before the pulse arrival. In (A) the errors are included within the data point size.](https://doi.org/10.1073/pnas.2316438121)
suggests that the dominant process is the structural disorder caused by the motion of the atoms induced by the rise in the lattice temperature by ultrashort laser pulses (38), known as the induced Debye–Waller effect consistent with the increase of the diffuse scattering background observed (SI Appendix). Similarly to the peak position shift response, the Bragg peak intensity does not fully recover to its initial state after 1.3 ns (SI Appendix). The long dynamics revealed by our data indicate the metastability of the induced 800 nm phase illustrating the complexity of the thermalization process in magnetite, involving multiple interplays of electron–electron, electron–phonon, and phonon–phonon scattering. Such lifetime is a signature of a hidden out-of-equilibrium phase which is supported by the unusual structural dynamics and the decrease in the intensity due to the phase separation between cubic and monoclinic islands.

We extend our investigation for hidden phases in magnetite by changing the energy of the optical excitation to 3.10 eV (400 nm). In Fig. 2B, different from the 800 nm case, we observe that the 400 nm laser pulses induce a 0.4% expansion of the lattice along the [110] direction, indicating a reinforcement of the monoclinic distortion. At 90 K, before excitation, the crystalline structure has a monoclinic angle $\beta_{M} = 90.236^\circ$ (21). The 400 nm induced expansion is a consequence of one out of three possible cases: i) an increase of the monoclinic tilt angle $\beta$, $\beta_{M} \text{400nm} > 90.236^\circ$, with unchanged lattice parameters $a$ and $b$. In this case, the point symmetry is invariant. ii) A change in the lattice parameter $a$ or/and $b$, with $\beta$ constant, leading to reduced symmetry. iii) A combination of both previous cases, leading as well to symmetry breaking. Ab initio calculations and optical data suggest that activating charge transfer enhances the coupling between phonons associated with the monoclinic tilt angle and the electronic ordering (26). For this reason, we conclude that the monoclinic tilt angle is the main contribution to the structural distortions we report.

Nevertheless, our data clearly show that the 400 nm optical excitation induces a lattice change that is opposite to the quasiadiabatic lattice response from our equilibrium data presented above (Fig. 1F), where the stabilization of the structure from 90 K down to 40 K shows no modification of the lattice parameters expected thermodynamically. Since the generated structure is not accessible thermally but only induced optically, we associate it with the emergence of a new hidden phase characterized by a monoclinic lattice with a tilting angle larger than the equilibrium value of 90.236° keeping the symmetry invariant, or a change in the lattice parameter leading to a reduced point symmetry or the combination of the two cases. The 400 nm induced hidden phase is also completely different from the one established by the 800 nm light. The first is firmly monoclinic, whereas the second is a mixture of monoclinic and cubic separated regions. The 400 nm structural hidden phase takes around 50 ps to emerge with only one direct expansion process, as presented in Fig. 2B, which we relate mainly to electron–phonon interaction. This new state lasts up to 300 ps without any recovery to the initial state giving it a metastable character. We observe a significant drop in the intensity response (Fig. 2D). For the 800 nm case, thermal effects and multiple scatterings from the mixed phase are the origins of the intensity drop. Although the decrease in intensity is consistent with the reduction of the structure factor for the (111)0.0 $\text{m}$ Bragg peak, it is surprising to observe a shrinking of the FWHM (SI Appendix), indicating a higher homogeneity in the atomic planes, which we cannot associate with a thermal-like behavior. This suggests that the new hidden structural state possesses a larger structural long-range order related to a larger monoclinic angle.

## 2. Discussion

The formation of distinct metastable hidden phases through two different photon energies demonstrates the critical role of electronic excitations in establishing nonequilibrium phases in magnetite as illustrated in Fig. 3. At LT, magnetite is stabilized in the insulating phase, resulting from a commensurate long-range order along the [001] direction (21, 36) of the trimerons network (22, 39) with a coherent length of (385±10) nm (14). In addition to the Jahn–Teller distortion caused by the orbital ordering (40), the electron localization within a trimeron unit produces a structural distortion in the Fe$^3+$ sites, where the distance between the central Fe$^3+$ and its two Fe$^3+$ nearest neighbors gets shorter, leading to a monoclinic distortion (21). This distortion has been confirmed by X-ray structure refinements (41), where it is found that fourteen over the sixteen nonequivalent trimerons have shown a shorter Fe$^3$–Fe$^3$ distance. When we illuminate magnetite with 800 nm photons (1.55 eV), we trigger d–d electronic excitations (16, 35, 42). They correspond to an electron delocalization from an occupied $t_2g$ of Fe$^3+$ to an unoccupied $t_2g$ orbital of Fe$^3+$ following the configuration $3d^53d^5 \rightarrow 3d^53d^6$. Prompting the d–d excitation restores the mobility of the minority spin $t_2g$ electrons and causes the valency to change for both Fe$^3+$ and Fe$^6+$ and, hence, alternates their sites inside the trimeron. Consequently, this local electronic fluctuation destroys the trimeron unit. According to out-of-equilibrium X-ray measurements, this destruction occurs in an ultrashort timescale < 300 fs (36). The destruction of trimerons yields the suppression of the long-range zigzag order connected at Fe$^3+$ sites. When the trimeron breaks, the Fe$^3$–Fe$^3$ distance returns to the high-temperature cubic equilibrium value. Hence, the structure relaxes, giving rise to the emergence of cubic phase islands inside the remaining monoclinic regions forming a phase separation that we qualify as an 800 nm metastable hidden phase.

The relaxation process to the equilibrium proceeds via electron–phonon and phonon–phonon scattering mechanisms. In some strongly correlated and layered systems, electrons primarily interact with optical phonons, which then anharmonically decay toward acoustic modes via a three-phonon scattering process (43–46). For magnetite, we can interpret the newly observed two steps in the relaxation process as the strong electron–phonon coupling involving the conduction electrons coupling with the $X_3$-driven mode (TO) for the first stage and the phonon–phonon coupling between $X_3$ (TO) and $\Delta_5$ (TA) modes for the second. This scenario is supported by recent UED data that have shown under similar photoexcitation (800 nm) that the $X_3$ (TO) mode is preferably triggered via the electron–phonon coupling (34) in the first few picoseconds. In addition, inelastic neutron scattering has shown that the $\Delta_5$ (TA) mode plays a primary role across the cubic-monoclinic transformation (24). However, the process is highly complex, and the involvement of other modes is likely. Further details are discussed in SI Appendix and in ref. 47.

When we photoexcite magnetite with the 400 nm (3.10 eV) light, we trigger multiple electronic excitations. The most dominant excitation is the charge transfer from 2p bands of oxygen to 3d bands of Fe$^3+$ (42). By activating the ligand-metal charge transfer, the oxygen ions of the octahedron FeO$_6$ supply electrons to the Fe$^{3+}$ nonparticipating ions, which consequently become Fe$^{2+}$. Hence, the proportion of Fe$^{2+}$ increases at the inactive trimerons B-sites, boosting $t_2g$ orbital ordering and creating extra trimerons, thus pushing beyond the limit of the thermodynamic maximum connectivity state leading to a new light-induced phase. This causes additional stress on the
magnetite structure provoked by cooperative effects. One is the Jahn–Teller distortion due to the extending $t_{2g}$ orbital ordering. At the same time, the second contribution comes from the shortening of the atomic Fe$_B$–Fe$_B$ distances induced by the charge localization within the newly formed trimerons (charge ordering) (21, 41). Recently, a high-accuracy X-ray experiment has shown that chemically doped magnetite introduces B site-selective Fe$^{2+}$ vacancies (which become Fe$^{3+}$) and weakens the trimeron long-range order (48). The authors attribute the vanishing of the VT in doped magnetite to the absence of the trimeron network. In our case, the 400 nm photodoping acts oppositely and provides additional electrons to the incomplete trimeron network. As our data clearly show, this results in an expansion of the lattice along the [110] direction. It is reasonable to speculate that the photodoping is site-selective, which orders and strengthens the trimeron crystal seen in the increase of the coherence length (Fig. 2F). In this scenario, the trimeron network can be seen as an imperfect Wigner crystal with homogeneous vacancies (inactive Fe$^{3+}$ B-sites). After 400 nm photodoping, the electrons from the oxygen ions activate the missing sites and complete the trimeron crystal enhancing the connectivity, which ultimately induces a monoclinic distortion favored by a strong electron–phonon coupling, in agreement with predictions from Borroni et al. (26).
3. Conclusion

Our results reveal the emergence of two distinct metastable hidden phases in magnetite. Starting from the same LT equilibrium state, we drive magnetite into two different structural states using two different photon energies. The 800 nm light induces d–d excitations, which favor the destruction of the trimerons and their network in a percolating fashion, leading to a phase separation between monoclinic-insulating regions and cubic-metallic islands. The 400 nm light triggers charge transfer between oxygen and iron at B-sites, which are found to be prolific for the trimerons and their arrangement, enhancing their connectivity, which leads to a stronger monoclinic distortion inaccessible adiabatically. Our findings demonstrate the key role of the trimeron structural configuration in magnetite and show the ability to establish hidden phases in quantum materials via specific electronic excitations in a strongly correlated environment.

4. Materials and Methods

Due to the nature of the electron, the scattering cross-section is larger than 4. Materials and Methods the trimeron structural configuration in magnetite and show the accessible adiabatically. Our findings demonstrate the key role of cubic-metallic islands. The 400 nm light triggers charge transfer trimerons and their network in a percolating fashion, leading induces d–d excitations, which favor the destruction of the states using two different photon energies. The 800 nm light libeqrium state, we drive magnetite into two different structural phases in magnetite. Starting from the same LT equi-

Author affiliations: "School of Basic Sciences, Institute of Physics, Laboratory for Ultrafast Microscopy and Electron Scattering, Ecole Polytechnique Federale de Lausanne, Lausanne CH-1015, Switzerland; 2) Dipartimento di Fisica, Politecnico di Milano, Milano 20133, Italy; 3) Department of Materials Science, Laboratory of Ultrafast Microscopy for Nanoscale Dynamics, University of Milano-Bicocca, Milano 20125, Italy; and 4) Centre national de la recherche scientifique, Laboratoire de Physique des Solides, Universite Paris-Saclay, Orsay 91405, France.