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Phonon-selective control of trimeron charge order in magnetite

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Abstract

Magnetite (Fe_3O_4) exhibits the Verwey transition, in which charge, orbital, and lattice degrees of freedom become intertwined in a trimeron-ordered insulating state. While the equilibrium properties of trimerons have been extensively studied, their selective nonequilibrium control remains largely unexplored. Here, we demonstrate phonon-selective manipulation of trimeron-associated charge order in epitaxial Fe_3O_4 thin films using intense terahertz excitation. Transient conductivity and optical spectroscopy reveal a pronounced frequency dependence: excitation below 4 THz drives the system toward the metallic state associated with the thermally induced Verwey transition, whereas excitation above 4 THz generates a distinct nonequilibrium metallic response. First-principles calculations identify low-frequency phonons that strongly perturb the Fe^{2+} - Fe^{3+} charge-ordering network and induce charge redistribution among the B-site Fe ions, thereby weakening trimeron-associated charge localization, providing a microscopic basis for the observed frequency-dependent electronic response. The strong frequency selectivity demonstrates that the transient state is governed not only by the deposited energy but also by the specific phonon mode excited. Our results establish phonon-selective excitation as a route for controlling trimeron-associated charge order and reveal how selective access to specific lattice degrees of freedom can control correlated nonequilibrium electronic states beyond the equilibrium pathway of the Verwey transition.

Main

Charge ordering is a central organizing principle in correlated electron materials, where the interplay between electronic correlations and lattice degrees of freedom can produce emergent ordered states and metal-insulator transitions. In such correlated materials, selectively driving specific degrees of freedom among the strongly intertwined electronic, lattice, spin, and orbital sectors to dynamically control collective order represents an important challenge in nonequilibrium quantum materials research¹. Among charge-ordered oxides, magnetite (Fe_3O_4) provides a particularly important example. Fe_3O_4 undergoes the Verwey transition at $T_V = 122\text{ K}$, across which its electronic, structural, and orbital degrees of freedom undergo a cooperative reconstruction^{2,3}. Above T_V , Fe_3O_4 adopts the cubic inverse-spinel structure, $(\text{Fe}^{3+})_A(\text{Fe}^{2+}\text{Fe}^{3+})_B\text{O}_4$, with mixed valence on the octahedral B sites. Below T_V , the crystal undergoes a symmetry-lowering structural transformation accompanied by a pronounced reduction in electrical conductivity (Fig. S1 of the Supplementary Information). The Verwey transition therefore represents a prototypical example in which charge localization is inseparably coupled to lattice and orbital degrees of freedom. A microscopic picture of this low-temperature charge-ordered state emerged from structural studies revealing that the nominal $\text{Fe}^{2+}/\text{Fe}^{3+}$ charge order cannot be described simply as a static arrangement of individual iron ions³⁻⁸. Instead, Senn et al. identified trimeron as fundamental correlated units of the low-temperature (LT) phase (Fig. 1a): linear three-Fe-site motifs involving a central Fe^{2+} -like site coupled to neighboring Fe^{3+} -like sites through characteristic Fe-Fe bond contractions and associated lattice distortions⁹. The trimeron picture established that charge localization in magnetite is inherently nonlocal and intimately connected to the underlying Fe-Fe network. Subsequent experimental and theoretical studies have further demonstrated that the electronic disproportionation associated with $\text{Fe}^{2+}/\text{Fe}^{3+}$ order is accompanied by characteristic structural distortions, emphasizing the cooperative nature of charge and lattice degrees of freedom in the Verwey state¹⁰⁻¹². Similar trimeron- and dimeron-based charge-ordering motifs have recently been identified in a variety of mixed-valence iron oxides, highlighting the broader importance of charge-cluster ordering in correlated materials¹³⁻¹⁸.

This intimate coupling between charge order and lattice structure suggests that selective excitation of lattice vibrations may provide a direct route to dynamically manipulate trimeron charge order. At the same time, this raises a broader question of whether electronic order in correlated materials with strongly coupled degrees of freedom can be controlled through selective access to specific lattice modes. The structural reconstruction at the Verwey transition involves a large number of symmetry-lowering distortions and low-energy lattice modes. Structural analyses based on X-ray and neutron scattering have shown that phonon modes at several points of the Brillouin zone, including the Γ , Δ , X, and W points, are involved in the distortion pattern that develops upon cooling^{19,20}. The resulting low-temperature structure is therefore not associated with a single lattice coordinate, but with a complex collective reconstruction. Ultrafast optical, x-ray, and electron diffraction studies have demonstrated that photoexcitation can destroy the charge-ordered Verwey state, induce transient metallic phases, and generate coherent phonons associated with the low-temperature structure of magnetite²¹⁻²⁴. However, in these experiments the lattice response was largely triggered indirectly through electronic excitation, making it difficult to disentangle the role of specific phonon coordinates in stabilizing trimeron order. To address this question, resonant excitation of infrared-active phonons has emerged as a powerful approach for controlling correlated materials far from thermodynamic equilibrium. In nonlinear phononics, selective driving of a lattice mode can produce large transient atomic displacements and thereby modify electronic interactions, structural order parameters, and collective phases on ultrafast timescales^{1,25-27}. In magnetite, the presence of low-frequency lattice modes associated with the structural distortions of the Verwey state suggests that such phonon-selective excitation may provide a direct means of

perturbing the Fe–Fe structural motifs underlying trimeron charge order. Importantly, this approach differs from conventional photoinduced control in which electronic excitations are generated first: resonant THz excitation can directly address the lattice coordinate itself.

Here, we demonstrate phonon-selective manipulation of trimeron-associated charge order in epitaxial Fe₃O₄ thin films. By selectively driving lattice modes that couple to the Fe²⁺-Fe³⁺ charge-ordering network, we access nonequilibrium states that cannot be understood simply as transient realizations of the thermally driven Verwey transition. Guided by first-principles calculations of lattice dynamics and electronic structure, we identify low-frequency phonons that strongly perturb the structural motifs underlying trimeron formation. We find that selective excitation of these modes produces a pronounced nonequilibrium electronic response, consistent with a transient weakening of trimeron-associated charge localization. Moreover, the response depends sensitively on the excitation frequency, demonstrating that the nonequilibrium electronic state cannot be understood solely in terms of deposited energy. These results establish phonon-selective excitation as a route to dynamically manipulate trimeron-associated charge order and reveal how selective lattice dynamics can drive magnetite away from the equilibrium pathway of the Verwey transition.

Characterization of the magnetite thin film

Figure 1b shows the THz conductivity of Fe₃O₄, evaluated with THz time-domain spectroscopy. The inset shows the temperature dependence of the conductivity at 1 THz, indicating the insulator-metal transition at 110 K. The conductivity spectra exhibit a gradual increase from the low-frequency side as the temperature increases above the Verwey temperature ($T_V \sim 110$ K), accompanied by Drude-like behavior at high temperatures. In addition, the phonon-related feature is observed, including a weak phonon absorption near 3 THz. Pimenov et al. analyzed the conductivity spectrum using spectroscopic ellipsometry and demonstrated that infrared-active phonons dominate the conductivity above 2 THz²⁸. These indicate that THz pulses with frequencies exceeding 2 THz are essential for selectively exciting phonon modes.

Figure 1c shows the optical density of Fe₃O₄ thin film at representative temperatures. One sees two absorption bands with peaks at 0.7 eV and 2.0 eV. Park et al. reported three absorption peaks at 0.6, 2, and 5 eV in reflection spectroscopy, which they respectively assigned to charge transfer (CT) transitions between Fe_B²⁺ t_{2g} and Fe_B³⁺ t_{2g} states, between Fe_B²⁺ t_{2g} and Fe_A³⁺ t_{2g} states, and between O 2p and Fe 3d states²⁹. Subsequent calculations have also associated the 2.0 eV peak with CT transitions between Fe_B²⁺ t_{2g} and Fe_B³⁺ e_g states³⁰. Importantly, both absorption peaks shift to lower energies at temperatures above the phase transition. In particular, the low-energy absorption band strongly influences the band gap, which governs the metal-insulator transition. The temperature dependence of the optical density at energies of 1.26 eV and 1.85 eV is shown in Fig. 1d. We add the temperature-dependent inverse of resistance in Fig. 1e, in which the observed hysteresis further confirms the high crystalline quality of the sample³¹. The optical density increases at 1.85 eV and decreases at 1.26 eV above T_V . These changes indicate that the Verwey transition can be effectively tracked by monitoring the optical density at these two energies, along with resistance change. The complete temperature dependence of the optical density and inverse of resistance for Fe₃O₄ thin film over the temperature range from 78–300 K is provided in Figs. S2a and S2b of the Supplementary Information.

Ab initio calculations for magnetite

We performed *ab initio* calculations to identify the phonon and electronic states of Fe_3O_4 in the THz frequency range, followed by a detailed analysis of phonon modes. For the structural parameters, we assumed the $\text{Fd}\bar{3}\text{m}$ cubic structure for the high-temperature (HT) phase, using data at 130 K³, and the Cc monoclinic structure for the LT phase, based on structural data at 20 K¹². Figure 2a shows the projected density of states (pDOS) for Fe^{3+} at the A site (tetrahedral), $\text{Fe}^{2+}/\text{Fe}^{3+}$ at the B site (octahedral), and oxygen. The calculated phonon dispersions are shown in Fig. S3 of the Supplementary Information. In the HT phase (Fig. 2a), there are 42 phonon modes in the 14-atom primitive cell. Group-theoretical analysis predicts four infrared-active T_{1u} modes, which are calculated at 4.82, 9.33, 9.68, and 16.05 THz. The pDOS indicates that phonon motion is dominated by Fe atoms at the B site below 5 THz, by Fe atoms at both the A and B sites between 5 and 10 THz, and oxygen atoms above 10 THz. In contrast, the LT phase contains 336 phonon modes due to the 112 atoms per unit cell, making the dispersion analysis substantially more complex. Nevertheless, the prominent features of the pDOS remain similar to those for the HT phase: Fe at the B site dominates below 4 THz, Fe at the A and B sites dominates between 5 and 10 THz, and oxygen dominates above 10 THz. These results indicate that low-frequency phonons below 4 THz predominantly involve B-site Fe displacement, suggesting that these modes can strongly perturb the Fe^{2+} – Fe^{3+} charge-ordering network.

We also calculated the electronic density of states (DOS) to support the interpretation of the optical spectra. Figure 2b shows the electronic pDOS. As discussed earlier, charge-transfer (CT) transitions between $\text{Fe}_B^{2+} t_{2g\downarrow}$ and $\text{Fe}_B^{3+} t_{2g\downarrow}$ states are important in the phase transition. Additionally, the optical transitions arising from other electronic states account for the characteristic absorption peak shifts to lower energy in the HT phase. These density functional theory (DFT) calculations support the use of changes in the visible-range optical spectrum as a probe of changes in the electronic states of Fe_3O_4 . They also suggest that the spectral shape may be modified by polaron contributions³². Although previous studies have proposed that infrared-inactive phonons at the Δ and X points, rather than the infrared-active phonons at the Γ point, play important roles in the equilibrium Verwey transition^{9,19-21}, the present THz-induced response can involve Γ -point phonons that directly perturb the Fe_B^{2+} – Fe_B^{3+} charge-ordering network and weaken trimeron-associated charge localization. In the low-symmetry Cc monoclinic structure, the selection rules are relaxed, allowing infrared-active phonons also to displace Fe atoms involved in trimeron formation. To investigate this effect, we calculated the changes in band gap, polarization, spin, and charge distribution induced by ionic displacements along each phonon mode involving B-site Fe ions. The atomic displacement amplitude was set to 0.2 Å, comparable to the magnitude of atomic displacements associated with the experimentally observed structural change across the Verwey transition.

Figure 3a shows the changes in polarization (ΔP) and spin (ΔS) of Fe at the B site for 80 phonon modes at the Γ point with frequencies below 6.0 THz. Among the modes with indices 0–30 (frequencies below 4.15 THz, red), many exhibit large and simultaneous changes in both ΔP and ΔS upon activation. In contrast, for modes with numbers 31 and higher (above 4.15 THz), neither polarization nor spin changes significantly. A summary of the atomic displacement effects on ΔP and ΔS is provided in Fig. S4 of the Supplementary Information. These findings suggest that low-frequency phonon-induced atomic rearrangements facilitate valence electron exchange between Fe^{2+} and Fe^{3+} at the B site, thereby weakening the $\text{Fe}^{2+}/\text{Fe}^{3+}$ charge disproportionation associated with trimeron charge order.

We focus here on phonon mode 17, highlighted as the large filled circle in Fig. 3a. The associated atomic displacements are illustrated in Fig. 3b. Figure 3c shows the $t_{2g\downarrow}$ orbital charge distribution when atoms are displaced along mode 17. This provides a more direct probe

of charge transfer than ΔS . In the equilibrium configuration, the $t_{2g\downarrow}$ orbital charge is localized on Fe_B^{2+} . However, as the atoms move along mode 17, the orbital charge partially delocalizes to Fe_B^{3+} , indicating partial charge transfer from Fe_B^{2+} to Fe_B^{3+} . These results demonstrate that this low-frequency mode below 4 THz modulates the trimeron-associated $\text{Fe}^{2+}/\text{Fe}^{3+}$ charge order through atomic displacements. Similar charge redistribution is also found for several other low-frequency modes that produce pronounced changes in polarization and spin, as illustrated for modes 9, 12, 14, and 16 in Fig. S5 of the Supplementary Information.

Experiments

We measured the resistance change of Fe_3O_4 thin films using a THz free-electron laser (THz-FEL), which enables selective induction of elastic phase transitions via phonon excitation³³. A schematic of the experiment is shown in Fig. 4a. The red curve in Fig. 4b shows the time profile of the voltage changes after THz-FEL pulse excitation. This voltage change corresponds to the current change through the sample, thereby allowing the monitoring of the resistance changes. The signal rises within the macropulse duration of 1 μs , and subsequently decays with a time constant of several microseconds. This response indicates an increase in conductivity, consistent with a transition from the insulating to the metallic phase. We varied the THz-FEL frequency from 3.3 THz to 5.2 THz, but no clear excitation frequency dependence was observed. Figure 4c shows the excitation pulse energy dependence of the peak voltage change. For both excitation frequencies, the signal shows a nonlinear increase when the excitation pulse energies exceed 0.3 mJ.

To further investigate the origin of this conduction behavior, we analyzed changes in optical density in the near-infrared and visible spectral regions. A schematic of this measurement is shown in Fig. 4d. The red curves in Fig. 4e show the time evolution of transmitted light intensity at 1.26 eV under THz-FEL excitation at 3.7 THz (upper) and 5.2 THz (lower). The prominent features of the signal are similar to those in Fig. 4b, with signals rising within 1 μs after THz-FEL pulse excitation and decaying over several microseconds. The decay constant is strongly temperature-dependent, becoming longer as the temperature approaches T_V . The positive signal corresponds to a reduction in the optical density of the Fe_3O_4 thin film, analogous to the change during the transition from the LT to HT phase. By comparing these optical density changes with the conductivity changes, we attribute the observed response to a redshift of the 0.7 eV absorption band under THz-FEL irradiation. This spectral shift shows little dependence on the excitation frequency.

In contrast, the transmitted light intensity changes at 1.85 eV exhibit a marked dependence on excitation frequency. The blue curves in Fig. 4e show the time evolution of the transmittance change at 1.85 eV for excitation at 3.7 THz (upper) and 5.2 THz (lower). At 3.7 THz, a distinct decrease in transmitted light intensity is observed, corresponding to an increase in optical density. The sign and spectral character of this response are consistent with a reduction of the $\text{Fe}^{2+}\text{-Fe}^{3+}$ charge disproportionation that stabilizes the trimeron-ordered state. Although the resulting electronic spectrum resembles that of the HT phase, the excitation is driven selectively through lattice modes coupled to the trimeron-associated charge-ordering network. In contrast, almost no change is detected at 5.2 THz. Since the optical density change at 1.85 eV is closely linked to the energy shift of the 2.0 eV absorption band, we interpreted these results as evidence that excitation at 5.2 THz may drive a distinct type of transition. Figure 4f shows the excitation pulse energy dependence of the peak transmittance changes. At 3.7 THz,

the signal increases nonlinearly above 0.4 mJ, whereas it remains tiny under 5.2 THz-FEL pulse excitation.

Figure 5 shows the temperature dependence of the optical density change in Fe₃O₄ thin films under THz-FEL excitation. The optical density change is apparent only at low temperatures, and the decay times of these signals gradually increase as T_V is approached. Notably, the optical density change at 1.85 eV is large only under low-frequency excitation below the critical temperature. We also performed the same experiment at an excitation frequency of 9.8 THz, and the results, shown in Fig. S6 of the Supplementary Information, closely resemble those at 5.2 THz. These findings support the conclusion that the 2.0 eV absorption band remains unaffected by THz-FEL excitation above 5 THz.

Discussion

Our experimental results show that the electronic state of insulating-phase Fe₃O₄ can be strongly modified by frequency-selective THz excitation. THz-FEL excitation below 4 THz induces a pronounced weakening of trimeron-associated charge localization, driving the electronic state toward a more delocalized metallic configuration. Although the resulting response shares characteristics with the HT phase, its strong frequency dependence indicates a distinct phonon-selective pathway. This frequency dependence indicates that the response is not governed only by the energy deposited into the system but is strongly influenced by the lattice mode excited by the THz pulse. In contrast, excitation above 4 THz produces a distinct nonequilibrium metallic response, suggesting that different phonon modes couple differently to the electronic degrees of freedom. These observations provide evidence that the lattice dynamics associated with trimeron charge order can be selectively manipulated on ultrafast timescales.

The possibility that the observed response originates from direct acceleration of charge carriers by the THz electric field must first be considered. The THz-FEL field reaches several hundreds of kV/cm, which is sufficiently strong to drive nonlinear electronic responses in some narrow-gap materials. Indeed, coherent impact ionization and carrier amplification have been reported under intense THz excitation in narrow-gap semiconductors^{34,35}. However, direct electronic acceleration is unlikely to account for the frequency-selective response observed here. The strong electronic correlations and short carrier scattering times in Fe₃O₄ suppress sustained coherent acceleration of the Fe t_{2g} electrons by a few-THz field. Moreover, metallic switching in VO₂ generally requires substantially larger electric fields, typically several MV/cm, and we have found no corresponding transition in VO₂ thin films under the same THz-FEL excitation conditions^{36,37}.

At the same time, the influence of electric fields on the Verwey state cannot be completely disregarded. Previous studies have demonstrated electrically driven resistive switching and electric-field control of the Verwey transition in Fe₃O₄, indicating that its charge-ordered state is intrinsically sensitive to strong electric fields^{38,39}. Nevertheless, such field-induced responses are primarily governed by the magnitude of the applied field. In contrast, the present experiments reveal a marked dependence on excitation frequency: while conductivity enhancement is observed over a broad frequency range, the characteristic optical response at 1.85 eV emerges predominantly for excitation below 4 THz. This pronounced frequency selectivity is difficult to reconcile with a purely field-driven mechanism. Instead, the observed behavior is consistent with a significant contribution from mode-selective lattice excitation. Fe₃O₄ possesses numerous low-energy phonon modes, and the 6-ps THz-FEL pulse provides sufficient temporal bandwidth for resonant coupling to these lattice vibrations. Together with

the first-principles calculations showing that low-frequency phonons strongly perturb the Fe^{2+} - Fe^{3+} charge-ordering network, the experimental results suggest that the nonequilibrium electronic state is governed by the interplay between strong-field excitation and selective lattice dynamics.

The calculated lattice distortions provide a microscopic basis for understanding this frequency-dependent response. Our first-principles calculations (Figs. 2 and 3) show that the low-frequency phonon modes induce characteristic distortions of the Fe-Fe network and a corresponding redistribution of charge among the B-site Fe ions. In particular, the Fe^{2+} - Fe^{3+} charge disproportionation associated with trimers is coupled to specific lattice displacements. When these lattice modes are resonantly driven to large amplitude, the associated Fe-Fe distances and local crystal fields are transiently modified, thereby perturbing the electronic states that stabilize the trimeron configuration. The experimentally observed response below 4 THz, which shares spectral characteristics with the high-temperature metallic phase (Figs. 1c,d and 4e), is therefore consistent with a transient weakening of trimeron-associated charge localization.

Importantly, the calculated phonon eigenvectors also contain substantial displacements of A-site ions, which are not directly involved in the Fe_3O_4 charge-ordering network. This observation indicates that the relevant phonon modes need not correspond simply to a local displacement of the trimeron itself. Rather, collective lattice motions can modify the Fe-Fe network indirectly through changes in the surrounding oxygen coordination and crystal structure. The resulting modulation of the B-site electronic states provides a mechanism by which phonon excitation can perturb trimeron-associated charge order. In this picture, the THz pulse does not simply heat the lattice toward the HT phase but also selectively drives specific lattice coordinates that destabilize the charge-ordered configuration. The frequency dependence of the transient conductivity and optical response therefore provides an experimental signature of mode-selective coupling between lattice dynamics and trimeron-associated charge order.

The distinction between phonon modes is particularly important in light of the complex trimeron configurations in the low-temperature monoclinic phase. Recent studies have classified trimers into different types, reflecting variations in their local $\text{Fe}^{2+}/\text{Fe}^{3+}$ configurations and structural environments³². The *Cc* phase contains characteristic Fe^{3+} - Fe^{2+} - Fe^{3+} and Fe^{2+} - Fe^{2+} - Fe^{3+} configurations, whose spatial arrangement contributes to the stability of the insulating state⁹. Selective excitation of different phonon modes can therefore perturb these local configurations to different extents. Our results suggest that phonon excitation below 4 THz preferentially weakens the Fe^{2+} - Fe^{3+} charge-ordering network and drives the system toward the electronic state associated with the HT phase, whereas higher-frequency excitation produces a distinct nonequilibrium state. Thus, the excitation frequency provides a control parameter for modifying the balance between lattice distortion and charge localization.

Taken together, our results establish a phonon-selective pathway for controlling trimeron-associated charge order in Fe_3O_4 . Rather than viewing the THz-induced transition simply as a photoinduced insulator-to-metal transition, our results indicate that the electronic transformation originates from selective perturbation of the lattice degrees of freedom that stabilize trimeron-associated Fe^{2+} - Fe^{3+} charge order. The ability to manipulate these microscopic charge-ordering units independently of the equilibrium structural pathway provides a new perspective on the lattice-charge coupling underlying the Verwey transition. More broadly, phonon-selective control may offer a route to manipulating competing charge,

orbital, spin, and lattice orders in correlated oxides and to accessing nonequilibrium states that are not available through conventional thermal control.

Methods

Sample preparation and characterization.

In our experiments, we used Fe₃O₄ films with thicknesses of 300 nm (and 1100 nm for THz conductivity measurement) epitaxially grown on MgO substrates. The films were prepared by pulsed laser deposition (PLD) using a Fe₃O₄ sintered target and an ArF excimer laser (193 nm)^{31,40}. The base pressure of the PLD chamber was approximately 1×10^{-6} Pa. Fe₃O₄ thin films were deposited under a partial oxygen pressure of 1.0×10^{-4} Pa, with the substrate temperature maintained at 640 K and the laser repetition rate set to 2 Hz.

For electrical transport measurements to confirm the Verwey transition properties, a pair of Au (35 nm)/Ti (5 nm) electrodes was patterned on the Fe₃O₄ films by sputtering using standard photolithography techniques. The temperature dependence of the resistance was measured with a physical property measurement system (PPMS, Quantum Design).

The Verwey transition properties were also confirmed using optical and THz spectroscopy. Optical density spectra were measured over the temperature range 80-300 K using a commercial spectrophotometer (JASCO, V570). To evaluate the THz conductivity in the frequency range 0.5-7 THz, THz time-domain transmission spectroscopy was performed on the thicker film over the temperature range 80-300 K, using an amplified Ti:sapphire laser (Spectra-Physics, Spitfire Pro). The temperature of the sample in both measurements was controlled using a liquid nitrogen cryostat (Cryo Industries of America, Inc.) equipped with plastic windows (Turupica).

Ab initio calculations.

Phonon calculations were performed using the finite-displacement method implemented in the phonopy program⁴¹, in combination with DFT calculations using the VASP code⁴². Atomic positions were optimized while the structural symmetry and lattice parameters were fixed to the experimental values; $a = b = c = 8.3904$ Å with Fd $\bar{3}$ m space group for the HT structure as measured at 130 K³ and $a = 11.8820$, $b = 11.8465$, $c = 16.7744$ Å, and $\beta = 90.2343^\circ$ with Cc space group for LT structure as measured at 20 K¹². After the atomic optimization, the structure was symmetrized using the ISOCIF code⁴³. The resulting CIF files are provided in the Supplemental Material. For the phonon calculations, the conventional cell containing 8 formula units (f.u.) was used for the HT structure, whereas the primitive cell containing 16 f.u. was adopted for the LT structure to reduce the computational cost. The Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation⁴⁴ was used for the exchange-correlation functional in the HT structure, with a $4 \times 4 \times 4$ k -point mesh. For the LT structure, the Hubbard- U correction (PBE+ U) was applied to reproduce the insulating charge-ordered phase with $U = 4$ eV applied to the Fe $3d$ orbitals^{20,45} using a $4 \times 4 \times 2$ k -point mesh. A ferrimagnetic configuration was considered with antiparallel spin orientation between Fe A and B sites. In the LT structure, the charge-order-induced ferroelectric polarization was calculated to be (3.14, -3.14, 5.12) $\mu\text{C}/\text{cm}^2$, in agreement with previous results⁴⁶.

Details of THz source.

The THz-FEL used in this study was based on the L-band electron linear accelerator at the Research Laboratory for Quantum Beam Science, SANKEN, the University of Osaka⁴⁷. The THz-FEL generates a linearly polarized THz pulse train consisting of ~ 30 micropulses with a temporal spacing of 37 ns (27 MHz repetition rate), forming a 1 μs macropulse. The macropulse

repetition rate was 5 Hz (time interval of 200 ms). The micropulse duration of 6 ps was evaluated with an electro-optic sampling technique using a synchronized Ti:sapphire laser³³. The maximum macropulse energy was set below 1 mJ, corresponding to 30 μ J per micropulse, and the excitation pulse energy was tuned using two wiregrid polarizers. With a 15-MeV electron beam, the FEL center frequency can be tuned from 2.8 THz to 8.0 THz by adjusting the wiggler magnet gap, and with an 18-MeV electron beam, the frequency range extends from 4 THz to 10.2 THz³³. The THz-FEL pulses were focused onto the Fe₃O₄ thin film using a gold-coated parabolic mirror with 50 mm focal length. The spot size of the THz-FEL pulse on the sample was approximately 0.3 mm. The estimated electric field of the THz pulse at the sample surface was about 2 MV/cm. However, the transmission loss of the cryostat plastic window and the Fresnel reflections at the sample surface must be considered. For a sufficiently thin film, the complex transmission coefficient at the boundary of high-refractive-index materials (such as Fe₃O₄ and MgO substrates) is less than 0.5. Consequently, the maximum electric field inside the sample is estimated to be < 1 MV/cm, which is below the critical field typically required to induce nonlinear responses in strongly correlated electron systems³⁶.

Details of time-resolved conductivity measurements.

Time-resolved conductivity measurements were performed on a Fe₃O₄ thin film at temperatures between 87 and 102 K using a liquid-nitrogen cryostat (Linkam Scientific Instruments) with plastic windows (Turupica). The Fe₃O₄ thin film sample was connected in series with a source meter (Keithley 2401) to apply a constant voltage of 1 V. Transient conduction profiles of Fe₃O₄ thin film were measured by monitoring voltage change across a 1 k Ω load resistance (R) using the digital oscilloscope (Teledyne LeCroy, Waverunner 640Z). To suppress noise originating from the linear accelerator, we recorded 50-shot waveforms of the voltage both with and without THz-FEL irradiation and obtained the averaged difference ΔV . The polarization of the incident THz-FEL pulses was set perpendicular to the direction of the electrode pair to avoid spurious short current caused by field electron emission from the electrodes³⁶. Substantial noise originating from the electrode surfaces was observed, as shown by the orange curves in Fig. 4b. To mitigate this effect, we applied a moving average to the acquired data, resulting in the red curves shown in Fig. 4b.

Details of time-resolved optical transmission measurements.

Time-resolved optical transmission measurements were performed on a Fe₃O₄ thin film at temperatures between 93 and 123 K using a liquid-nitrogen cryostat (Linkam Scientific Instruments) equipped with plastic windows (Turupica). Continuous-wave visible (670 nm) and near-infrared (980 nm) laser diodes (Thorlabs, CPS670F and CPS980S, respectively) served as probe light sources. The two probe beams were combined coaxially using a pellicle beam splitter and focused onto the sample with an off-axis parabolic mirror. The transmitted probe light was detected by a high-speed photodetector (Thorlabs DET10A), and waveforms were acquired over 50 shots using a digital oscilloscope (Teledyne LeCroy, Waverunner 640Z). In the measurements shown in Fig. 4, we first examined the dependences of the transient response on excitation frequency and excitation pulse energy at a fixed sample temperature. We then switched the probe wavelength, followed by systematic measurements as a function of temperature.

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Contributions

A.N.H. directed the scientific research, prepared the sample with R.R., A.I.O. and H.T., performed the irradiation experiments together with R.R. and M.N., analyzed the data with M.N. and wrote the initial draft of this manuscript with R.R. and M.N. K.Y. and T.O. calculated

the phonon modes and electronic states of Fe_3O_4 . All authors contributed to the discussions for this manuscript and wrote parts of the manuscript.

Ethics declarations**Competing interests**

The authors declare no competing interests.

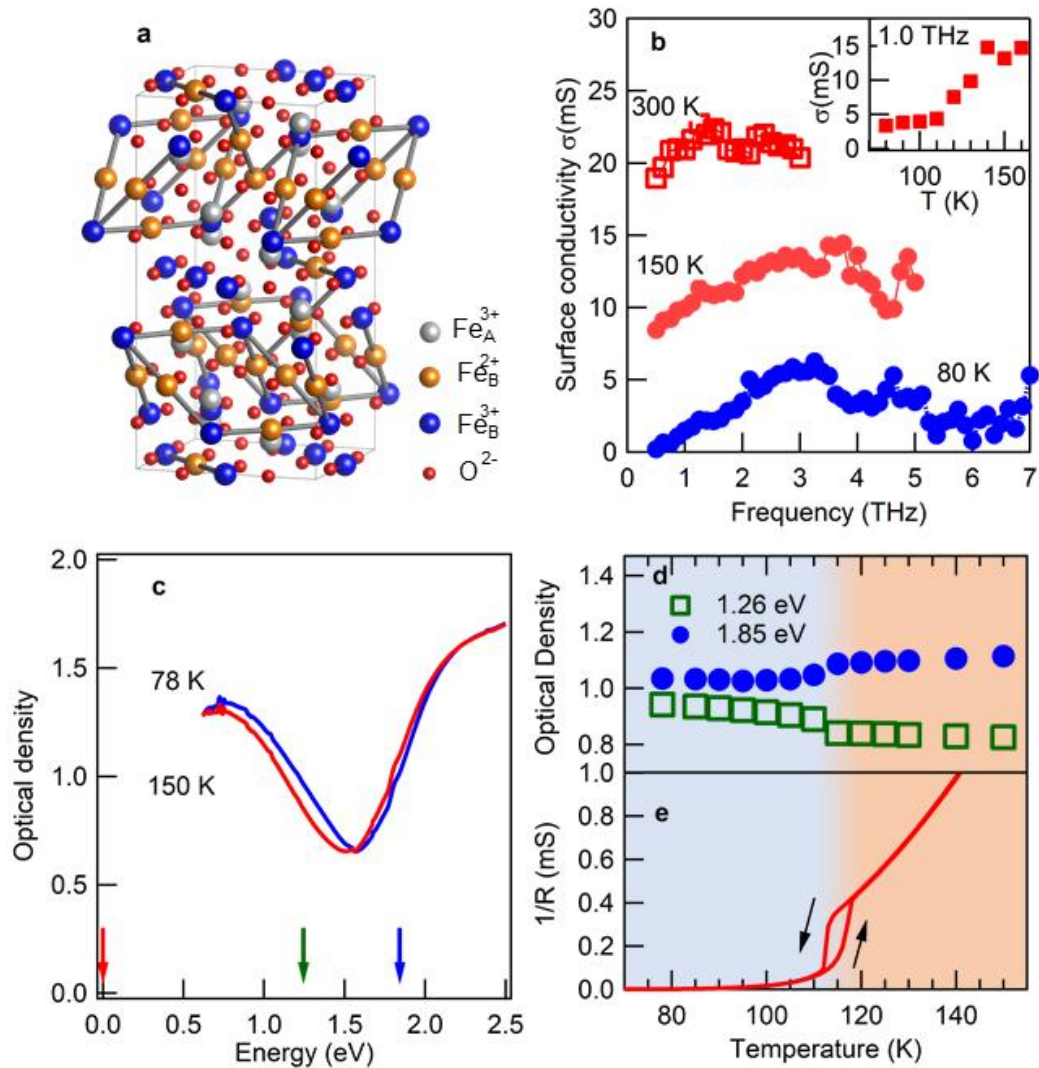


Figure 1| Electrical and optical properties of magnetite thin films. **a** Atomic arrangement of LT Fe_3O_4 in the Cc monoclinic phase. The grey bonds indicate trimeron formation. **b** Real part of the optical conductivity of a 1100 nm-thick Fe_3O_4 film, measured by THz time-domain spectroscopy. The inset shows the temperature dependence of the real part of the optical conductivity at 1 THz. **c** Optical density of a 300 nm-thick Fe_3O_4 film. Colored arrows indicate the photon energies corresponding to panels d and e. **d** Temperature dependence of the optical density at 1.26 eV and 1.85 eV for the Fe_3O_4 thin film during the heating process. **e** Inverse electrical resistance of the Fe_3O_4 film as a function of temperature

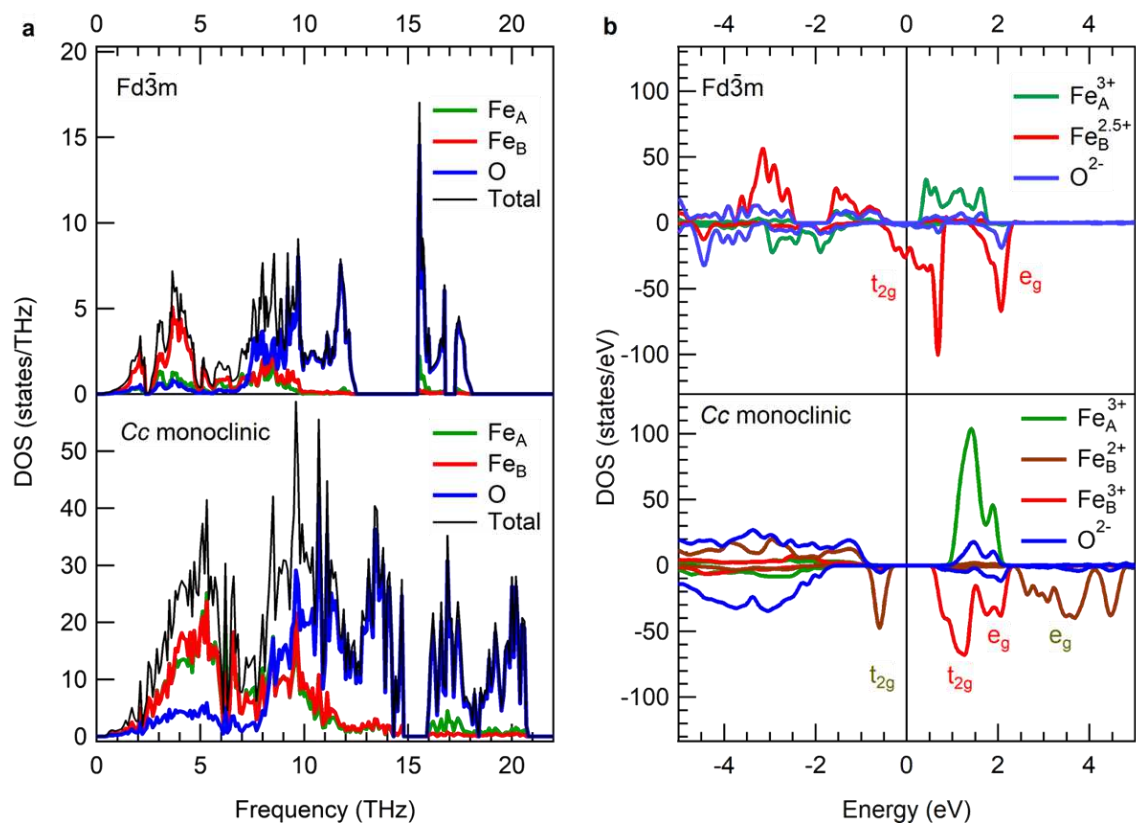


Figure 2| Ab initio calculations for magnetite. a Phonon pDOS for HT (Fd $\bar{3}$ m cubic, upper) and LT (Cc monoclinic, lower) Fe_3O_4 . **b** Electronic pDOS for Fe_3O_4 .

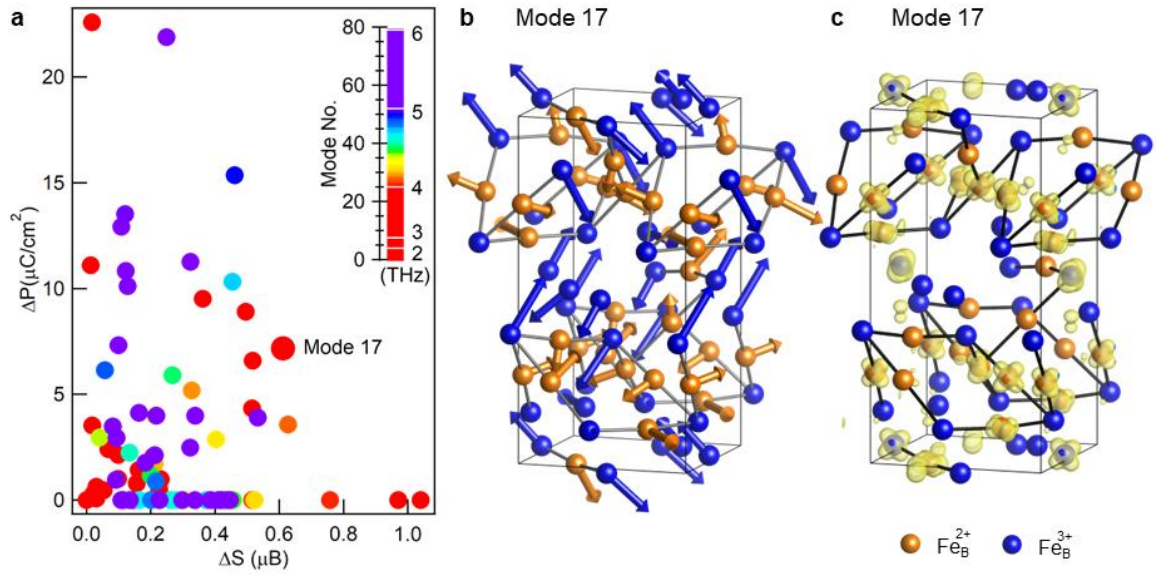


Figure 3| Changes in physical properties induced by specific phonon atomic displacements. **a** Changes in spin (ΔS) and polarization (ΔP) induced by a static 0.2 Å atomic displacement along each phonon mode. The colour of the filled circles represents the phonon mode index, as indicated by the colour scale bar. **b** Atomic displacement vectors for mode 17 (3.75 THz) of Fe_3O_4 in the Cc monoclinic structure. The black bonds represent trimers. **c** $\text{Fe}_B^{2+} t_{2g\downarrow}$ orbital charge distributions for a structure with a static 0.2 Å displacement applied along mode 17.

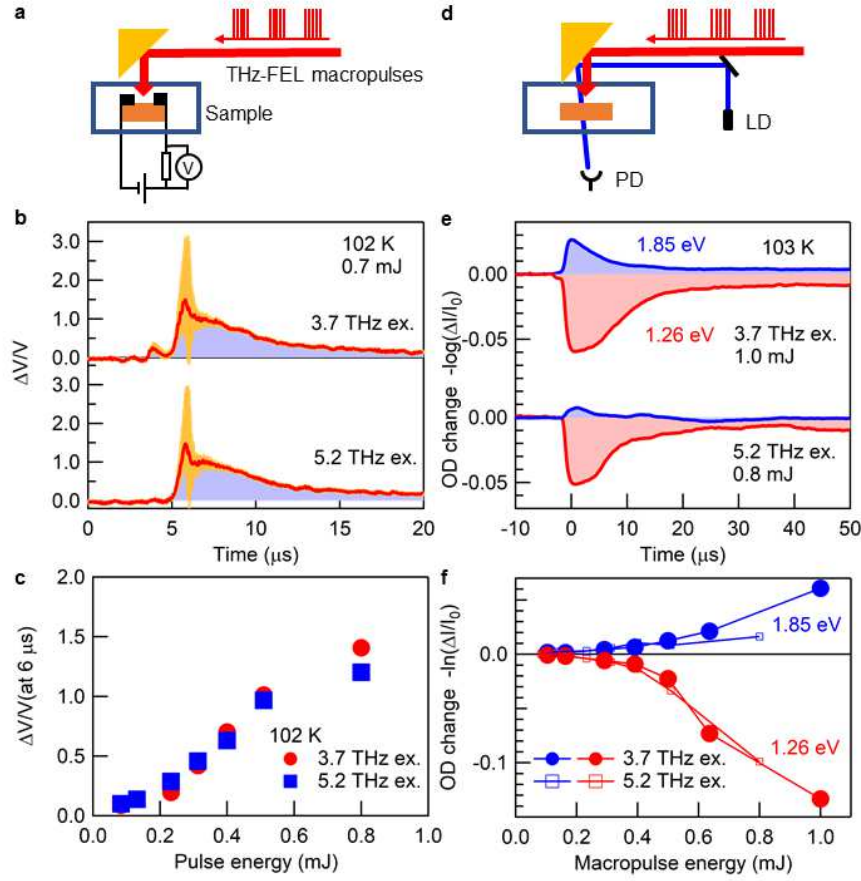


Figure 4| Time profiles of conductivity and optical density changes in magnetite thin films under THz-FEL excitation. **a** Schematic of the transient conductivity measurement. **b** Time evolution of voltage changes following THz-FEL pulse excitation at 3.7 THz (upper) and 5.2 THz (lower). The orange curves are the original acquired data, including electrode noise, and the red curves show the average data. **c** Excitation pulse energy dependence of the peak voltage changes. **d** Schematic of the transient optical density measurement. **e** Time profiles of transmitted light intensity changes at 1.26 eV (red curves) and 1.85 eV (blue curves) under THz-FEL excitation at 3.7 THz and 5.2 THz. **f** Excitation pulse energy dependence of the peak optical density change.

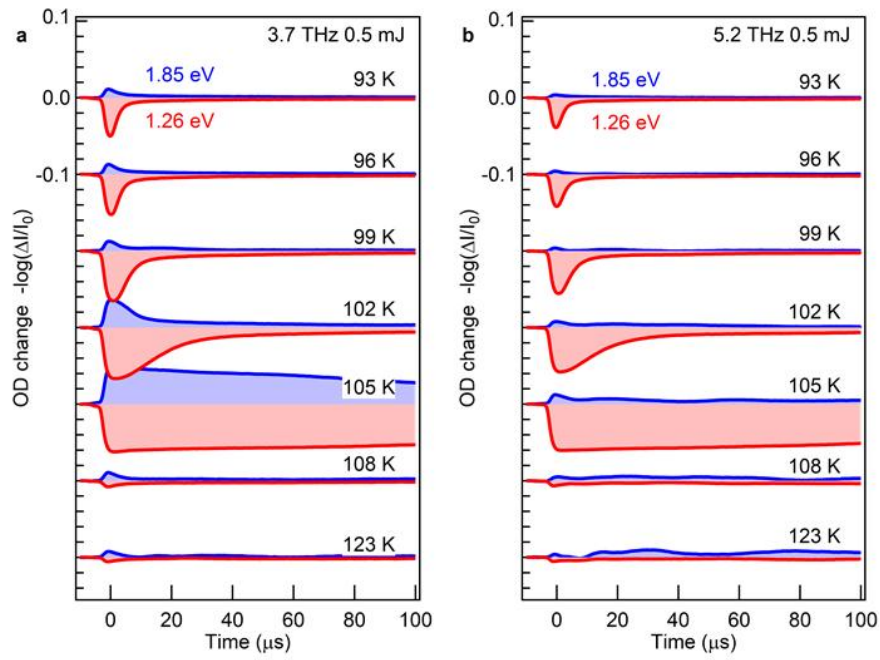


Figure 5| Temperature dependence of the optical density changes in magnetite thin films under THz-FEL excitation. **a** Optical density changes in Fe_3O_4 thin films under 3.7 THz excitation at the temperatures from 93 to 123 K. **b** Optical density changes under 5.2 THz excitation.

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