Discovery of the soft electronic modes of the trimeron order in magnetite

Edoardo Baldini,1,† Carina A. Belvin,1,† Martin Rodriguez-Vega,2,3 Ilkem Ozge Ozel,1 Dominik Legut,4 Andrzej Kozłowski,5 Andrzej M. Oleś,6,7 Przemysław Piekarz,8 José Lorenzana,9 Gregory A. Fiete,1,3 and Nuh Gedik1,∗

1Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
2Department of Physics, The University of Texas at Austin, Austin, Texas 78712, USA
3Department of Physics, Northeastern University, Boston, Massachusetts 02115, USA
4IT4Innovations Center, VSB-Technical University of Ostrava, 17.listopadu 15, 708 00 Ostrava, Czech Republic
5Faculty of Physics and Applied Computer Science, AGH-University of Science and Technology, Aleja Mickiewicza 30, PL-30059 Krakow, Poland
6Marian Smoluchowski Institute of Physics, Jagiellonian University, Prof. S. Lojasiewicza 11, PL-30348 Krakow, Poland
7Max Planck Institute for Solid State Research, Heisenbergstraße 1, D-70569 Stuttgart, Germany
8Institute for Nuclear Physics, Polish Academy of Sciences, Radzikowskiego 152, PL-31342 Krakow, Poland
9Institute for Complex Systems, National Research Council and Department of Physics, University of Rome “La Sapienza,” I-00185 Rome, Italy

(Dated: January 22, 2020)

The Verwey transition in magnetite (Fe₃O₄) is the first metal-insulator transition ever observed [1] and involves a concomitant structural rearrangement and charge-orbital ordering. Due to the complex interplay of these intertwined degrees of freedom, a complete characterization of the low-temperature phase of magnetite and the mechanism driving the transition have long remained elusive. It was demonstrated in recent years that the fundamental building blocks of the charge-ordered structure are three-site small polarons called trimers [2]. However, electronic collective modes of this trimeron order have not been detected to date, and thus an understanding of the dynamics of the Verwey transition from an electronic point of view is still lacking. Here, we discover spectroscopic signatures of the low-energy electronic excitations of the trimeron network using terahertz light. By driving these modes coherently with an ultrashort laser pulse, we reveal their critical softening and hence demonstrate their direct involvement in the Verwey transition. These findings represent the first observation of soft modes in magnetite and shed new light on the cooperative mechanism at the origin of its exotic ground state.

Along with his groundbreaking discovery in 1939, Verwey postulated the emergence of a charge ordering of Fe²⁺ and Fe³⁺ ions as the mechanism driving the dramatic conductivity drop at $T_V \sim 125$ K [1]. A vast number of subsequent experimental and theoretical investigations, including those by Anderson [3], Mott [4], and many others, have stimulated a still unresolved debate over a complete description of the Verwey transition [5, 6]. In particular, several seemingly incompatible findings related to the intricate low-temperature phase of magnetite have been reported: the crucial role of Coulomb repulsion [7], the necessity of including electron-phonon coupling [4, 8, 9], small charge disproportionation [7, 10, 11], anomalous phonon broadening with the absence of a softening towards $T_V$ [12], and the observation of structural fluctuations that are connected to the Fermi surface nesting [13] and that persist up to the Curie transition temperature ($T_C \sim 850$ K) [14].

The last decade witnessed significant progress in understanding the Verwey transition from a structural point of view. Most notably, a refinement of the low-temperature charge-ordered structure as a network of three-site small polarons, termed trimers, was given by X-ray diffraction [2] (Fig. 1a). A trimeron consists of a linear unit of three Fe sites accompanied by distortions of the two outer Fe³⁺ ions towards the central Fe²⁺ ion. An orbital ordering of coplanar 2py orbitals is also established on each ion within the trimeron (Fig. 1b). This picture of the trimeron order has been crucial for determining the correct noncentrosymmetric $Cc$ space group of magnetite and explaining its spontaneous charge-driven ferroelectric polarization [2, 6, 15]. Nevertheless, despite extensive research, no soft modes of the trimeron order have been detected to date. Unveiling novel types of collective modes in the low-temperature phase of magnetite and their critical softening would significantly shape our understanding of the long-sought cooperative phenomenon at the origin of the Verwey transition.

Here, we use time-domain terahertz (THz) spectroscopy (Fig. 1c) to reveal the electronic modes of the trimeron order. Their signature is imprinted on the equilibrium optical conductivity of the material in an energy-temperature range previously unexplored. We establish their involvement in the Verwey transition by driving them coherently with an ultrashort near-infrared laser pulse and mapping their softening with a delayed THz
FIG. 1. Trimeron order in magnetite and experimental methodology. a, The low-temperature charge-ordered structure of magnetite as a network of trimerons, small polarons that extend over three linear Fe sites. The purple and black spheres represent Fe$^{3+}$ and Fe$^{2+}$ ions, respectively. b, Each trimeron consists of two outer Fe$^{3+}$ ions and one central Fe$^{2+}$ ion (the arrows depict distortions of the lattice). This charge ordering is accompanied by an ordering of coplanar $t_{2g}$ orbitals on each Fe site within the trimeron. The surrounding oxygen ions are shown in red, and the gray spheres represent Fe sites that do not participate in the trimeron. (a and b are adapted from Ref. [2].) c, Schematic of the experimental setup. Time-domain THz spectroscopy in a transmission geometry is used to determine the low-energy optical conductivity of the sample in equilibrium (without the pump beam). To examine its dynamics, an ultrashort near-infrared (1.55 eV) pump pulse sets the system out of equilibrium and a weak, delayed THz probe pulse measures the pump-induced change in the optical conductivity.

Figure 2a shows the real part of the low-energy optical conductivity ($\sigma_1$) measured in equilibrium on a magnetite single crystal. Slightly below $T_V$, the spectrum displays a broad, featureless continuum (red curve), which previous studies attributed to a power-law behavior expected in the presence of charge hopping between polaronic states [16]. As the temperature is lowered well below $T_V$ to a hitherto unexplored regime (pink and blue curves), the continuum in the optical conductivity is suppressed and two Lorentzian lineshapes clearly emerge. These excitations slightly harden with decreasing temperature and are centered around 1.5 and 4.2 meV at 7 K. Since they appear below the charge gap for single-particle excitations [17], it is natural to ascribe them to distinct low-energy collective modes at the Brillouin zone center. Intriguingly, these excitations have never been observed in any previous study on magnetite [16, 18–22]. Thus, it is pivotal to identify their origin and clarify their potential involvement in the Verwey transition.

We make use of advanced density-functional theory (DFT) calculations of the phonon dispersions in the low-temperature $Cc$ symmetry of magnetite to compare the energy of the two observed excitations with that of long-wavelength lattice modes (see Methods and Supplementary Note 2). The lowest-lying optical phonons at the $\Gamma$ point of the Brillouin zone have symmetries $A'$ and $A''$ and correspond to the folded $\Delta_5$ mode of the cubic phase. Their energy of 8 meV is in excellent agreement with inelastic neutron [19, 25] and x-ray [12] scattering data. Therefore, the low-energy modes in our experiment cannot be assigned to phonons. Similarly, magnon dispersions measured by inelastic neutron scattering do not show any long-wavelength spin waves with energies in our spectral range [18]. Since ferrimagnetism in magnetite is quite robust (with $T_C \sim 850$ K), these excitations would be expected to persist at high temperature [16]. Finally, according to the Kugel-Khomskii Hamiltonian (which describes well the details of the orbital order in magnetite [7]), orbitons can be readily ruled out because their energy scale is of the same order as magnons. Thus, after ruling out these scenarios, the only remaining possibility is that the detected modes are collective excitations of the trimeron order.

We now clarify whether these collective modes play a key role in the Verwey transition by unraveling their critical behavior. This is a challenging task to accomplish under equilibrium conditions, as the broad conductivity continuum seen in Fig. 2a obscures any spectroscopic signature of the collective modes at temperatures proximate to $T_V$. It is thus unclear whether the modes persist as strongly damped Lorentzians buried under this continuum and how their peak energy varies with temperature. To overcome this experimental difficulty, we illuminate our magnetite crystal with an ultrashort near-infrared laser pulse and drive its collective modes coherently [26]. We vary the laser fluence absorbed by our sample, exploring a regime that allows us to transiently increase the lattice temperature but not completely melt the trimeron order [23, 24] (see Supplementary Note 5). We then mon-
Observation of low-energy electronic collective modes and their critical softening. a, Real part of the equilibrium optical conductivity ($\sigma_1$) of magnetite in the THz region. The spectrum near $T_V$ (red curve) exhibits a broad, featureless continuum that rises with a power-law behavior, in accordance with a previous report [16]. Lowering the temperature reveals two Lorentzian lineshapes (pink and blue curves) that are due to collective modes. b, Pump-induced change in the THz electric field ($\Delta E$) transmitted through the sample at 7 K following photoexcitation at various absorbed fluences. The traces are offset vertically for clarity. Each curve was fit to two damped sine waves and the fits in the time domain are displayed as dashed black lines. c, Energy of each oscillation extracted from the fits as a function of fluence. At low fluence, the energies are close to those in a at 7 K, so the oscillations correspond to the same collective modes present in equilibrium. Both energies soften with increasing fluence, demonstrating their involvement in the Verwey transition. d, Amplitude of each mode versus fluence. The inset shows the linear rise of the amplitudes in the low fluence regime, which is compatible with an impulsive Raman excitation process. The shaded bars in c and d indicate the critical fluence for melting the trimeron order as reported in Refs. [23, 24].
To rationalize the behavior of these coherent collective modes after photoexcitation, we develop the simplest time-dependent Ginzburg-Landau model compatible with the symmetries of the system. In our calculations, we consider electronic collective mode fluctuations described by a complex order parameter \( \psi = |\psi|e^{i\varphi} \). In the Ginzburg-Landau potential \( F = F[\psi] \), we include a nonlinear term arising from electronic interactions, a linear coupling term between the real and imaginary parts of \( \psi \) responsible for inversion symmetry breaking, and a pinning potential arising from impurity effects. The nonequilibrium action of the pump pulse on the mode fluctuations is introduced through a coupling to the intensity of the pump electric field. The full dynamics of the system are described by equations of motion that include phenomenological relaxation and inertial terms for both \( |\psi| \) and \( \varphi \) (details of the Ginzburg-Landau model are given in the Methods and Supplementary Note 8). Despite its simplicity, our model captures the salient features of our experiment data. Specifically, the energies of both \( |\psi| \) and \( \varphi \) soften towards \( F_C \) (Fig. 4a) and the oscillation amplitudes of the modes rise linearly with increasing fluence before experiencing a dramatic quench in the proximity of \( F_C \) (Fig. 4b). Furthermore, there is a crossing of the amplitudes of the modes around \( 0.5F_C \), which is also present in the experimental data (see Fig. 2d). The resulting time dependences of \( |\psi| \) and \( \varphi \) are plotted in Figs. 4c and 4d, respectively, for several fluence values. While our model successfully reproduces the qualitative behavior of the experimentally observed dynamics, some quantitative mismatch is still present. In particular, deviations from the observed quasi-mean-field behavior of the mode energies in Fig. 2c is due to the exact energy-fluence functional form used to describe the thermodynamic properties of the material (see Supplementary Note 8).

Our results are rather surprising given the current understanding of magnetite’s low-temperature phase. Since in this material the charge order is commensurate with the lattice and the Verwey transition is thought to be of an order-disorder type based on the observation of overdamped (i.e. diffusive) modes [13, 21, 29, 30], the detection of underdamped (and therefore propagating) soft electronic modes is unexpected. This apparent contradiction can be reconciled by recalling that the trimeron order in magnetite leads to the development of a spontaneous ferroelectric polarization [2, 6, 15]. The ferroelectric instability is of the electronic (improper) type and involves charges that are weakly bound to the underlying lattice [6]. Low-energy modes can naturally emerge as collective fluctuations of charges within the trimeron network on top of the robust commensurate charge order. Though our observed modes seem reminiscent of the electronic component of amplitudons and phasons in conventional charge-density wave systems, such a simplified picture is not expected to capture the complexity of the trimeron order in magnetite. It seems more plausible that the internal structure of these excitations involves tunneling of polarons through the potential barrier separating neighboring Fe sites [15]. An estimate of the energetics of this process (see Supplementary Note 3) confirms that such a polaron excitation lies in our THz range. Only the development of advanced theoretical models will contribute to the identification of the actual real-space pattern characterizing these collective charge fluctuations,
FIG. 4. Time-dependent Ginzburg-Landau theory describing the dynamics of the collective modes. a,b, Dependence of the energies (a) and amplitudes (b) of both components of the order parameter (|ψ| and ϕ) as a function of pump fluence. c,d, Evolution of |ψ|(t) (c) and ϕ(t) (d) in the time domain over a range of fluences. The calculated behavior matches the qualitative trends observed in the experiments (see Fig. 2b–d), namely the softening of the energies and the initial linear increase in the amplitudes followed by their destabilization towards the critical fluence $F_C$.

as their extremely low energy hinders their investigation with probes of the charge dynamics other than THz spectroscopy and high-resolution Raman scattering.

The current study highlights the strength of ultrafast THz probes in uncovering the soft character of electronic collective modes associated with an intricate order, in line with recent experiments on the Higgs and Leggett modes in superconductors [31, 32]. Beyond these results, we envision the use of strong THz fields [33] to resonantly drive the modes of the trimeron order in magnetite and similar charge-ordered compounds, enabling the coherent control of electronic ferroelectricity.

METHODS

Single crystal growth and characterization. A single crystal of synthetic magnetite oriented in the (111)-direction with a thickness of 0.5 mm was used in all experiments. The crystal was grown using the skull melting technique from 99.999% purity Fe$_2$O$_3$. Afterwards, the crystal was annealed under a CO/CO$_2$ gas mixture to establish the appropriate iron-oxygen ratio. AC magnetic susceptibility was used to characterize the sample and determine the value of $T_V$ (see Supplementary Note 1).

Time-domain and ultrafast THz spectroscopy. A Ti:Sapphire regenerative amplifier system with 100 fs pulses at a photon energy of 1.55 eV and repetition rate of 5 kHz was used to generate THz pulses via optical rectification in a ZnTe crystal. The THz signal transmitted through the sample was detected by electro-optic sampling in a second ZnTe crystal with a 1.55 eV gate pulse. The frequency-dependent complex transmission coefficient was determined by comparing the measured THz electric field through the magnetite crystal to that through a reference aperture of the same size, and the complex optical parameters were then extracted numerically [34].

For the ultrafast THz measurements, the output of the laser was split into a 1.55 eV pump beam and a THz probe beam, with the THz generation and detection scheme described above. The time delay between pump and probe and the time delay between the THz probe and the gate pulse could be varied independently. To measure the spectrally-integrated response, the THz time was fixed at the peak of the THz waveform and the pump-probe delay was scanned. The spectrally-resolved measurements were obtained by scanning both the THz time and the pump-probe delay time.

DFT calculations. The crystal and electronic structure of the material was optimized using the projector augmented-wave method [35] within the generalized gradient approximation [36] implemented in the VASP program [37]. The full relaxation of lattice parameters and atomic positions was performed in the crystallographic cell of the $Cc$ structure containing 224 atoms. The strong electron interactions in the Fe(3d) states have been included within the local density approximation (LDA)+U method [38] with the Coulomb interaction parameter $U = 4.0$ eV and the Hund’s exchange $J = 0.8$ eV. The phonon dispersion curves were obtained using the direct method [39] implemented in the Phonon software [40]. The same approach was previously employed to study phonon dispersions in the cubic $Fd\bar{3}m$ [9, 41] and monoclinic $P2/c$ [30] structures of mag-
netite. The Hellmann-Feynman forces were calculated by displacing all non-equivalent 56 atoms from their equilibrium positions along the positive and negative \( x, y, \) and \( z \) directions, and the force-constant matrix elements were obtained. The phonon dispersions along the high-symmetry directions in the first Brillouin zone were calculated by the diagonalization of the dynamical matrix.

**Time-dependent Ginzburg-Landau calculations.** We constructed the simplest Ginzburg-Landau potential that captures phenomenologically the physics of the charge order in magnetite and is compatible with the symmetries of the system (see Supplementary Note 7). We defined the complex order parameter as \( \psi = |\psi|e^{i\varphi} \), which is related to the real-space charge-density wave as \( \delta \rho(r) = \text{Re}\{\psi e^{i\mathbf{q} \cdot \mathbf{r}}\} \), where the wave vector could correspond to any linear combination of all the symmetry-allowed wave vectors. We modeled the transition as weakly first order, with a Ginzburg-Landau potential given by

\[
F[\psi, \varphi] = \frac{a}{2} |\psi|^2 + \frac{b}{4} |\psi|^4 + \frac{d}{2} |\psi|^2 \sin \varphi + \frac{g}{2} \cos \varphi + F_i, \tag{1}
\]

where \( a(T) = -A(T_V - T) \) and \( g(T) = -G(T_V - T) \) are functions of temperature and \( b > 0 \) for stability. A non-zero amplitude-phase interaction term \( d \) is allowed due to the lack of inversion symmetry in the low-temperature phase. The fourth term, proportional to the coefficient \( g \), corresponds to a phenomenological "restoring force" that could arise from a pinning potential originating in short-range impurities [42–45]. This term could also emerge from a linear coupling with phonon modes belonging to the same irreducible representation as the charge modulation, where the proportionality constant \( g \) would be a function of the electron-phonon coupling constant [46, 47]. Finally, the coupling to the laser field was given by \( F_i = E(t)^2(\eta_\psi |\psi|^2 + \eta_\varphi \varphi^2) \), where \( \eta_\psi \) and \( \eta_\varphi \) are coupling constants. The pump electric field \( E(t) \) was modeled as \( E(t)^2 = 2F/(\epsilon_0 T_p) \delta T_p(t) T_p \), where \( F \) is the absorbed pump laser fluence, \( c \) is the speed of light, \( \epsilon_0 \) is the permittivity of free space, \( \delta T_p(t) \) is a broadened delta function, and \( T_p \approx 0.1 \) ps is the pump pulse duration. The functional form used for the coupling to the laser field was chosen to mimic the force acting on the collective modes within the impulsive stimulated Raman scattering framework [26].

**DATA AVAILABILITY**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**ACKNOWLEDGMENTS**

Work at MIT was supported by the US Department of Energy, BES DMSE, Award number DE-FG02-08ER46521 and by the Gordon and Betty Moore Foundation’s EPiQS Initiative grant GBMF4540. C.A.B. and E.B acknowledge additional support from the National Science Foundation Graduate Research Fellowship under Grant No. 112374 and the Swiss National Science Foundation under fellowships P2ELP2-172290 and P400P2-183842, respectively. M.R.-V. and G.A.F. were primarily supported under NSF MRSEC award DMR-1720595. G.A.F also acknowledges support from a Simons Fellowship. A.M.O is grateful for the Alexander von Humboldt Foundation Fellowship (Humboldt-Forschungspreis). A.M.O. and P.P. acknowledge the support of Narodowe Centrum Nauki (NCN, National Science Centre, Poland), Projects No. 2016/23/B/ST3/00839 and No. 2017/25/B/ST3/02586, respectively. D.L. acknowledges the project IT4Innovations National Supercomputing Center CZ.02.1.01/0.0/0.0/16_013/0001791 and Grant No. 17-27790S of the Grant Agency of the Czech Republic. J.L. acknowledges financial support from Italian MAECI through the collaborative project SUPERTOP-PGR04879, bilateral project AR17M07, Italian MIUR under the PRIN project Quantum2D, Grant No. 2017Z8TS5B, and from Regione Lazio (L.R. 13/08) under project SIMAP.

**AUTHOR CONTRIBUTIONS**

E.B. conceived the study. C.A.B., E.B., and I.O.O. performed the experiments. C.A.B. and E.B. analyzed the experimental data. A.K. grew the magnetite single crystals. P.P., D.L., and A.M.O performed the density functional theory calculations. M.R.-V. and G.F. performed the time-dependent Ginzburg-Landau calculations. J.L. contributed to the data interpretation. C.A.B., E.B., and N.G. wrote the manuscript with crucial input from all other authors. This project was supervised by N.G.

**COMPETING INTERESTS**

The authors declare no competing interests.

**MATERIALS AND CORRESPONDENCE**

Correspondence and requests for materials should be addressed to N.G.
Supplementary Information for “Discovery of the soft electronic modes of the trimeron order in magnetite”

Supplementary Note 1: Single crystal characterization

Figure S1 shows the real part of the AC magnetic susceptibility $\chi'$ as a function of temperature from 117 K to 126 K for the magnetite single crystal used in these measurements. The sudden decrease in $\chi'$ around 123 K indicates that $T_V \sim 123$ K for this sample. This drop in the susceptibility results from microtwinning of the crystal when it undergoes its structural transition from cubic to monoclinic at $T_V$. In the low-temperature monoclinic phase, the ferroelastic domains constrain the motion of magnetic domain walls due to a higher cost in elastic energy. Consequently, the value of $\chi'$ should be lower in the monoclinic phase compared to the cubic phase [48]. The temperature at which $\chi'$ exhibits this discontinuity therefore corresponds to $T_V$.

FIG. S1. AC magnetic susceptibility of our magnetite crystal. Real part of the AC magnetic susceptibility $\chi'$ as a function of temperature. From the temperature at which $\chi'$ undergoes a sudden drop, we obtain $T_V \sim 123$ K for this crystal.

Supplementary Note 2: Phonon dispersion calculations in the Cc structure

In this section, we present density-functional theory (DFT) calculations of the phonon dispersion in the low-temperature phase of magnetite. In the Cc structure, there are 336 phonon modes at each wave vector. Figure S2a shows the calculated phonon dispersion curves in the low-energy range up to 20 meV. These calculations are in excellent agreement with experimental measurements of the phonon energies using inelastic neutron [19, 25] and x-ray [12] scattering (symbols). Figure S2b displays the calculated partial phonon density of states projected on the Fe sites (black curve), which agrees well with experimental data taken from Ref. [49] (red curve).

FIG. S2. DFT calculation of the phonon dispersion in the Cc structure. a, Low-energy phonon energy-momentum dispersion curves of magnetite calculated for the monoclinic Cc symmetry. The symbols mark the energies of the phonon modes measured experimentally by inelastic neutron scattering (violet symbols from Ref. [25] and red symbols from Ref. [19]) and inelastic x-ray scattering (green symbols from Ref. [12]). There are no optical phonon branches in the energy range of the two newly-observed collective modes (1−4 meV). b, Partial phonon density of states projected on the Fe sites. The results of the DFT calculations are shown in black, while the experimental results at 50 K (taken from Ref. [49]) are in red.
Supplementary Note 3: Additional discussion about the assignment of the collective modes

As indicated in the main text, we can rule out the possibility that the collective modes observed in equilibrium (Fig. 2a) are due to optical phonons or folded acoustic phonons by comparing our data to ab initio calculations of the phonon dispersion in the $Cc$ structure of magnetite (Fig. S2a). The calculated dispersion reveals that there are no optical phonon branches at the $\Gamma$ point in the energy range corresponding to the two observed modes. The lowest-energy zone-center mode (i.e. $\Delta_5$) finds excellent agreement with inelastic neutron scattering data [19]. Folded acoustic phonons (obtained by a folding of the Brillouin zone) likewise have much higher energies than our two modes.

As for the oscillations in the time domain, their energies are very close to those of the two collective modes in equilibrium at 7 K, indicating that they are indeed the same modes. In this case, we also rule out any alternative explanation associated with phonons. It is important to consider the possibility that the observed oscillations in the time domain are coherent acoustic phonons (CAPs) generated by the pulse pulse through the deformation potential or the thermoelectric coupling [50]. The absence of any dispersion in the spectrally-resolved data excludes this scenario. Indeed, when the probe photon energy is tuned in a spectral range where the material is highly transparent (i.e. typically below the fundamental optical gap), the Brillouin scattering condition $\lambda_{\text{photon}} = \frac{\lambda_{\text{coh}}}{2n}$ holds [51]. If the refractive index $n$ is roughly constant across the probed range (as is the case here - see Supplementary Note 4A), then the wavelength of the coherent strain should depend on the probe photon energy. As we do not observe any variation in the frequency of the oscillations at different probe photon energies (see Fig. 3), the oscillations cannot be CAPs. Furthermore, CAPs typically exhibit a cosine behavior as a function of time (due to the nature of the generation process [50]), whereas the oscillations in our experiment are closer to sine functions. The latter is indicative of a scenario in which the force acting on the collective modes is more impulsive than displacive in nature [26].

In addition to the discussion of magnons in the main text, we note that folded acoustic magnetic modes can be ruled out as well due to their energies not falling in our energy range [18]. Also, the frequency of the spontaneous ferromagnetic resonance in magnetite is $\sim 16$ GHz [52], which is extremely low.

Finally, we argue that a plausible explanation for the existence of the observed electronic modes involves tunneling of polarons that give rise to the electrical polarization. Specifically, we assume that a polaron can tunnel from one Fe site to the neighboring one with a matrix element $t_{\text{eff}}$. In this model, the excitations observed experimentally stem from the bonding-antibonding splitting $\Sigma = 2t_{\text{eff}}$. From Fig. 3 of Ref. [15] we observe that in the 16 f.u. unit cell (112) atoms there are four such polarons: Two of the Fe$^{3+}$-type (labeled B14 and B14′) and two of the Fe$^{2+}$-type (labeled B12 and B12′). We consider a tunneling process through these sites. As a proxy to the single polaron barrier, we compute within DFT the barrier in which all four polarons move coherently to the next nearest neighbor site along the $a$-axis. This effectively produces a mirror image of the structure with the height of the barrier determined by symmetry by the energy difference between the non-polar $P2_1/c$ structure and the polar $Cc$ structure. We obtain that the barrier height is 87 meV per polaron, which agrees with the value that can be deduced from previous studies [15]. Next, we interpret this as the binding energy of a polaron ($E_p$) in a Holstein-like model. Using a Lang-Firsov transformation [53, 54], we can estimate the matrix element for coherent polaron hopping as $t_{\text{eff}} = t e^{-E_p/\omega_0}$, where $t$ is the bare electron hopping integral and $\omega_0$ is the effective phonon frequency. We evaluate the energy scale associated with this process by substituting the relevant parameters for magnetite. The main displacements to stabilize the polaron are due to the oxygen atoms surrounding the polaron sites. Projecting the phonon density of states on these polaron Fe sites, we find a low-energy peak around 20 meV (Fig. S2b). We interpret this as the characteristic phonon energy $\omega_0$. We extract the value of the direct Fe $d$-$d$ hopping from our DFT calculations, which yield a value of $t \sim 200$ meV. The latter is in agreement with a simple estimate that can be given by the Harrison method [55], considering an Fe-Fe distance of 2.97 Å. As a result, we obtain $\Sigma \sim 5.2$ meV, a value that lies on the same energy scale of the modes observed experimentally.

Supplementary Note 4: Additional equilibrium data

A. Refractive index at 7 K

The refractive index was extracted from the equilibrium THz data as described in the Methods section. Figure S3 displays the real part of the refractive index ($n$) in the THz region shown in Fig. S3. The index exhibits very little variation across this energy range and can therefore be approximated as constant.

B. Equilibrium optical conductivity at 100 K

As discussed in the main text, our equilibrium optical conductivity data at 100 K agrees very well with previously reported measurements of the THz conductivity of magnetite in this temperature regime, in which a power-law dependence is observed and attributed to hopping.
Supplementary Note 5: Transient effective lattice temperature and heat diffusion

In this section, we connect the pump laser fluence ($F_0$) with a rise in the effective lattice temperature ($T$) after photoexcitation. The fluence effectively deposited into the sample is

$$F = F_0(1 - R)(1 - e^{-z/\lambda_p}),$$

where $R$ is the sample reflectivity, $\lambda_p = 330$ nm is the penetration depth for 1.55 eV photons, and $z$ labels the direction of light propagation. Energy conservation imposes a relation between fluence and temperature,

$$F = \frac{m}{A} \int_{T_i}^{T_f} C_p(T) dT,$$

where $A$ and $m$ are the sample area and mass (determined by the penetration depth $\lambda_p$) illuminated by the pump laser, respectively, $T_i = 7$ K is the temperature of the sample prior to the pump pulse arrival, $T_f$ is the effective temperature reached after photoexcitation, and $C_p(T)$ is the temperature-dependent heat capacity at constant pressure. In a solid, due to the negligible change in volume during the heating process, the heat capacity at constant pressure and at constant volume are expected to be very similar.

Equation (S2) can be solved numerically for $T_f$. Using data of the heat capacity of a synthetic magnetite crystal taken from Ref. [56] (Fig. S5a), we obtain $T_f$ as a function of fluence (Fig. S5b). According to this estimate, the effective temperature after photoexcitation rises to 124 K for the maximum fluence used in the experiment ($F_{\text{max}} = 3.0$ mJ/cm$^2$), a temperature that is approximately equal to $T_V$.

The time evolution of the transient lattice temperature is given by the heat diffusion equation,

$$\partial_t \left( \rho \int_{T_i}^{T_f} C_p(T) dT \right) = \nabla \cdot (\kappa(T) \nabla T(t, z)), \quad (S3)$$

subject to the initial condition $T(0, z) = T_f$ if $z < \lambda_p$ and $T(0, z) = T_i = 7$ K otherwise, and insulating boundary conditions $\partial_z T(t, z)|_{z=0,L} = 0$. In Eq. (S3), $\rho = 5.175$ g/cm$^3$ is the sample density and $\kappa$ is the temperature-dependent thermal conductivity. Given that the sample is nearly uniformly illuminated along the plane, we consider only the spatial dimension along the depth of the sample. We solve Eq. (S3) for $T(z, t)$. The results, shown in Fig. S6, demonstrate that the effective temperature changes only slightly in the vicinity of the photoexcited region in the time scale relevant for the experiments.

---

**FIG. S3.** Refractive index of magnetite at low temperature. Real part of the refractive index ($n$) measured by time-domain THz spectroscopy at 7 K. There is almost no variation in the index over this energy range.

**FIG. S4.** Power-law dependence of the low-energy optical conductivity just below $T_V$. Real part of the optical conductivity ($\sigma_r$) in the THz range at 100 K from Fig. 2a. At low energies (inset), the curve is fit to a power law with exponent $s = 1.8$, in close agreement with previously reported THz measurements [16].
FIG. S5. **Relationship between pump laser fluence and effective sample temperature.** 

a, Heat capacity data used in the calculation of the effective temperature taken from Ref. [56]. 

b, Effective temperature as a function of laser fluence obtained by solving Eq. (S2). The dashed line indicates the maximum fluence used in the experiments.

FIG. S6. **Heat diffusion through the sample.** Effective temperature as a function of position $z$ in the sample at three different times. The gray dashed line corresponds to the temperature profile immediately after photoexcitation. In these calculations the full diffusion equation is solved, taking into account the temperature dependence of $C_p$ and $\kappa$. The penetration depth is $\lambda_p = 330$ nm, while the sample depth is $L = 0.06$ cm.

**Supplementary Note 6: Additional pump-probe data and analysis**

**A. Second data set of the pump fluence dependence**

In Fig. S7a, we provide a second data set of the fluence dependence of the pump-induced THz electric field ($\Delta E$) at 7 K. Though the oscillations show slight differences compared to those in Fig. 2b, the qualitative behavior is the same, specifically the softening of the mode energies (Fig. S7b) and the initial linear rise in the amplitude of the modes followed by a decrease towards the critical fluence, as well as a crossing of the amplitudes of the two modes (Fig. S7c).

**B. Fits of the pump-probe response in the time domain**

As discussed in the main text, we fit the pump-probe response in the time domain using two damped sine waves. First, we show that a single damped sinusoid is not sufficient to describe the data. Figure S8 shows the pump-probe response at low and high fluences for both data sets with fits to a single damped sinusoid (red dashed lines) and two damped sinusoids (blue dashed lines). There is poor agreement between the data and the fits to a single oscillation, demonstrating the presence of more than one oscillation frequency. Instead, we can see that the sum of two damped oscillations is able to capture the salient features of the data. We remark that, while the fit matches the oscillations extremely well at initial pump-probe delay times, at later times there are slight deviations. These may be due to slight variations in the sample temperature caused by heat diffusion (see Fig. S6). The fits were performed by taking into account the time resolution of the experiment, noting that the observed dynamics are a convolution of the oscillation model with the pump and probe pulse profiles (see Chapter 9 in Ref. [57]).

We further note that the dynamics of the damped oscillations can be accurately tracked due to the lack of any relaxation background in the temporal trace. The latter is typically expected from the excitation and subsequent relaxation of charge carriers that are photodoped above the optical gap ($E_G \sim 200$ meV) [17, 24]. Its absence sig-
FIG. S7. Second data set of the pump fluence dependence. a. Second data set of the pump-induced change in the THz electric field (\(\Delta E\)) transmitted through the sample at 7 K following photoexcitation at various absorbed fluences. The traces are offset vertically for clarity. Each curve was fit to two damped sine waves and the fits in the time domain are displayed as dashed black lines. b. Energy of each oscillation extracted from the fits as a function of fluence. c. Amplitude of each mode versus fluence. The inset shows the linear rise of the amplitudes in the low fluence regime, which is compatible with an impulsive Raman excitation process. The shaded bars in b and c indicate the critical fluence for melting the trimeron order as reported in Refs. [23, 24].

FIG. S8. Fits of the pump-probe response in the time domain. a, b. Pump-probe response at low fluence (a) and high fluence (b) for the data set in Fig. 2b. c, d. Pump-probe response at low fluence (c) and high fluence (d) for the data set in Fig. S7a. The fits to one (red) and two (blue) damped sine waves are shown for each curve. A single oscillation is unable to capture all the features of the data, demonstrating that two frequencies, and therefore two coherent modes, are present at all fluences.

Confirms that, within the time resolution of our experiment (~100 fs), the excited charge carriers localize and assume a polaronic character, similar to what is observed in other correlated insulators governed by strong electron-boson coupling [58].
C. Fourier transform analysis of the pump-probe response

A Fourier transform analysis confirms the results of the fits in the time domain. Figure S9 shows the Fourier transform of the two data sets with the fits to the mode energies (red and violet dots) superposed on the curves. It can be observed that the two methods for determining the energies of the modes agree well within the resolution of the Fourier transform and the error bars of the fits. This provides further evidence for the presence of two modes at all fluences.

![FFT plots](graph.png)

**FIG. S9. Fourier transform of the temporal traces.** a, Fourier transform analysis of each trace in Fig. 2b of the main text. It is difficult to distinguish the two modes due to their close energies and large broadening. The red and violet dots represent the energies of the two collective modes obtained from the fits in Fig. 2c. The two methods for determining the energies of the modes agree well within the resolution of the Fourier transform and the error bars of the fits. b, Fourier transform analysis of each trace in Fig. S7a along with the mode energies from the fits in Fig. S7b. In this data set, it is easier to see two distinct peaks at higher fluences. As seen from both the fits in Fig. S8 and the Fourier transforms here, together these two data sets provide strong evidence for the presence of two coherent collective modes at all fluences.

D. Pump polarization dependence

In order to assign the symmetry of the modes, we perform a pump polarization dependence (Fig. S10a). The oscillations remain unchanged as the pump polarization is varied from parallel to perpendicular to the probe polarization. This isotropic response of the pump-probe signal indicates that the observed modes are totally symmetric. The same dependence was seen at all pump fluences. We also investigated the response to a circularly polarized pump (Fig. S10b) and found that the same oscillations as in Fig. S10a are present and do not change when the pump helicity is varied.

E. Pump-probe response with 3.10 eV excitation

We also repeat the pump-probe experiments with a pump photon energy of 3.10 eV, using a BBO crystal to frequency double the 1.55 eV light from the laser. For this pump photon energy, which is close to the charge-transfer transition, we observe very similar oscillations to those excited by the 1.55 eV pump pulse (Fig. S11a). Despite our ~100 fs time resolution, the Fourier transform of the oscillations at this photon energy (Fig. S11b) shows no signature of the totally-symmetric optical phonon modes in the range of 13.9 to 25.9 meV that have been observed in a previous study using a pump excitation of 3.10 eV [30]. This demonstrates that the spectral region of our THz probe is solely sensitive to the newly-discovered low-energy electronic modes.

Supplementary Note 7: Group theory aspects of the Verwey transition

In this section, we perform a group theory analysis of the Verwey transition in magnetite in order to construct the simplest time-dependent Ginzburg-Landau (GL) model that is compatible with the symmetries of the system (see Supplementary Note 8). In a phase transition from a high symmetry ($G$) to a low symmetry ($G_0$) space group, it is crucial to identify the irreducible representations (IRs) that lead to the symmetry breaking $G \rightarrow G_0$. This defines an inverse Landau problem [59, 60]. In magnetite, the space group above $T_V$ is $Fd\bar{3}m$ ($O_h^6, 227$), with cubic crystal symmetry and point group $O_h$. Below $T_V$, the space group becomes $Cc$ ($C_s^4, 9$), with monoclinic crystal symmetry and point group $C_s$ [2, 15]. Therefore, we seek the IRs that lead to the symmetry breaking $Fd\bar{3}m \rightarrow Cc$. We solve this problem with the aid of the software packages GET_IRREPS [61–63] and ISOTROPY [64]. The transformation $\mathcal{T}$ relating the basis vectors of both phases is [65]

$$
\mathcal{T} = \begin{pmatrix}
1 & -1 & 0 \\
1 & 1 & 0 \\
0 & 0 & 2
\end{pmatrix}.
$$

(S4)

The isotropy subgroups are listed in Table S1, along with the IRs and corresponding wave vectors. The main result is that none of the IRs give the low-temperature subgroup $Cc$. Therefore, we need at least two IRs to couple and condense in order to drive the transition. In principle, there are multiple choices of order parameters (OPs) that can drive the symmetry breaking $Fd\bar{3}m \rightarrow Cc$, as seen in the graph of isotropy subgroups shown in Fig. S12. From group theory arguments alone is not possible to determine which are the relevant IRs as all possible paths are allowed. However, experimental observations [66] and a previous group theory analysis [9] have identified that...
FIG. S10. **Pump polarization dependence.** a, Pump-probe response for different angles of the pump polarization. There is no change in \( \Delta E \), indicating that the modes are totally symmetric. b, Response to a circularly polarized pump. The oscillations are identical when the pump beam is right and left circularly polarized (RCP and LCP) and linearly polarized as in no change in \( \Delta E \).

FIG. S11. **Response to 3.10 eV photoexcitation.** a, Pump-probe response when the pump photon energy is 3.10 eV (blue curve). The oscillations are very similar to those excited by the 1.55 eV pump (red curve). b, Fourier transform of both curves in a. There are no features at higher energies where a previous study observed totally-symmetric optical phonon modes excited by 3.10 eV light [30]. Our THz probe is therefore only sensitive to the low-energy electronic collective modes reported here.

\( Pmc2_1 \cap Cm \), corresponding to coupling the OPs \( X_3 \) and \( \Delta_5 \) in a particular direction in representation space, generates the \( Cc \) space group symmetry. Additionally, phonon modes with the symmetries \( \Gamma, \Delta, X \), and \( W \) have been identified to participate in the transition [2], and all these IRs appear in Table S1, in agreement with the experimental observations.

Based on the result that a coupling between the IRs \( X_3 \) and \( \Delta_5 \) allows for the symmetry breaking \( Fd3 \to Cc \), some insight can be gained by studying the space group representation at the wave vectors \( \Delta \). The star of the \( k \)-vector \( X \) (obtained by applying the point group operations of \( O_h \) to \( X \)) in the Brillouin zone has three arms: \((1,0,0), (0,1,0), \) and \((0,0,1)\) in units of \( 2\pi/a \), where \( a \) is the lattice constant in the high temperature cubic unit cell. Since these \( k \)-vectors are related by symmetry operations, the corresponding states are equivalent [67]. The group of the wave vector has 16 symmetry operations (not listed here) and four two-dimensional IRs \( X_i \) for \( i = 1,2,3,4 \) [68]. Among these four IRs, we assume that only \( X_3 \) participates in the transition with OP direction \((\eta_1, \eta_2, -\eta_2, -\eta_1, \eta_3, -\eta_3)\) in representation space as obtained with ISOTROPY (the dimension of representation space is defined by the number of arms in the star of \( k \) times the dimension of the IR of the little group [68]). The arbitrary real constants \( \eta_i \) with \( i = 1,2,3 \) generate a three-dimensional subspace. From the direction of the OP in representation space, the wave vectors \( q_i^\parallel = (1,0,0), q_2^\parallel = (0,1,0), \) and \( q_3^\parallel = (0,0,1) \) could be involved in the distortions causing the phase transition.

On the other hand, the star of the \( k \)-vector \( \Delta = (0,2u,0) \) with \( u = 1/4 \) has six arms: \((\pm 1/2,0,0), (0,\pm 1/2,0), \) and \((0,0,\pm 1/2)\). The group of the wave vector has 48 symmetry operations and
TABLE S1. Irreducible representations that participate in the Verwey transition. List of IRs, isotropy subgroups, and k-vectors between the parent group Fd3m and Cc.

| IRs  | Isotropy subgroup |
|------|-------------------|
| Γ1   | Fd3m (227)        |
| Γ4   | I41/amd (141)     |
| Γ3   | C2/m (12)         |
| Γ2   | C2/m (12)         |
| Γ1   | Fd3m (216)        |
| Γ4   | I4m2 (119)        |
| Γ3   | Cm (8)            |
| Γ5   | Ima2 (46)         |

Using these results, we now construct an invariant polynomial under the space group operations of the high-symmetry group that couples the IRs X3 and Δ5 [64, 69], consistent with previous experimental observations [2, 23, 66, 70, 71]. The allowed terms in the polynomial are, to second-order, \( F^{(2)} = |X|^2 + |\Delta|^2 \), where \( X = (X_1, X_2, X_3) \) and \( \Delta = (\Delta_1, \Delta_2) \). The only allowed third-order term is \( F^{(3)} = X_1 X_2 X_3 \), while the fourth-order terms are

\[
F^{(4)} = |X|^4 + |\Delta|^4 + |X|^2|\Delta|^2 + (4X_1^4 + X_2^4 + 6X_2^2X_3^2 + X_3^4) + (X_2^2 + X_3^2)(4X_1^2 + X_2^2 + X_3^2) + X_1^2(\Delta_1^2 + \Delta_2^2) + (X_2^2 - X_3^2)\Delta_1 \Delta_2 + (X_1^2 + X_3^2)\Delta_2^2 + (\Delta_1^4 + \Delta_2^4) .
\]

This polynomial, which is the basis of a formal GL potential for the transition, involves five OPs related to the wave vectors that could, in principle, be involved in the transition. However, our experimental measurements are not momentum-resolved so the polynomial derived here is not directly relevant. Therefore, in the next section, we construct a minimal GL potential based on this formal polynomial to describe the transition.

Supplementary Note 8: Effective time-dependent Ginzburg-Landau model

Here, we present the results of the time-dependent GL calculations. The GL potential compatible with the symmetries of magnetite is described in the Methods section. Below \( T_{V} \), \(|\psi|^2\) acquires a finite expectation value denoted \( \psi_0 \) such that \( |\psi(t)|^2 = 1 + 2\psi_0|\delta \psi(t)| + O((\delta \psi(t)/\psi_0)^2) \). Due to the phase-amplitude mixing allowed by the lack of inversion symmetry, the laser also couples directly to the phase \( \phi \) in the dynamics, we include both relaxation and inertial terms for the amplitude and phase and allow them to have different relaxation rates \( \gamma_\psi \) and \( \gamma_\phi \). The effective temperature \( T(t) \) is in general a function of time and laser fluence \( F \). However, due to the expected slow heat diffusion, as calculated in Supplementary Note 5, we will assume that it remains at its initial effective value after photoexcitation during the whole measurement, \( T(t) = T_f \) for \( z < \lambda_p \). The differential equations governing the system are obtained by taking the variation of the GL potential with respect to the amplitude and phase around their equilibrium positions \( \psi_0 \) and \( \phi_0 \). We obtain

\[
\frac{\partial^2 |\psi|}{\partial t^2} + \gamma_\psi \frac{\partial |\psi|}{\partial t} + a(T)|\psi|^2 + b|\psi|^3 + d|\psi|^2|\varphi| = \eta_\psi E(t)^2 \psi_0 ,
\]

\[
\frac{\partial^2 \varphi}{\partial t^2} + \gamma_\varphi \frac{\partial \varphi}{\partial t} + g(T) \varphi = \eta_\varphi E(t)^2 \varphi_0 .
\]

We solve the coupled differential equations (S5) and (S6) numerically.

The energies of the amplitude \(|\psi|\) and phase \( \varphi \) (Fig. 4a) and their maximum amplitudes (Fig. 4b) as a function of pump laser fluence are given in the main text. Figures 4c,d illustrate the behavior of the OPs \(|\psi|\) and \( \varphi \), respectively, as a function of time for a range of fluence values. The parameters used in all the plots are \( A/b = 0.13 \text{ K}^{-1} \), \( G/b = 0.032 \text{ K}^{-1} \), \( \gamma_\psi/b = 0.5 \), \( \gamma_\varphi/b = 0.4 \), \( \eta_\psi/\eta_\varphi = 0.505 \), and \( d/b = 2.8 \).
FIG. S12. **Group theory analysis of the Verwey transition.** Graph of isotropy subgroups obtained with the software suite GET_IRREPS for the symmetry breaking $Fd\bar{3}m \rightarrow Cc$. Red boxes highlight the subgroups corresponding to IRs of the high-symmetry group.
et al. [11] Subías, G.

[14] Perversi, G. et al.

[13] Bosak, A. et al.

[10] Wright, J. P., Attfield, J. P. & Radaelli, P. G. Long range

[16] Pimenov, A. et al.

[18] McQueeney, R. J. et al.

[19] Borroni, S. et al.

[20] Huang, H. Y. et al.

et al. [4] Mott, N. F. Materials with mixed valency that show a

Senn, M. S., Wright, J. P. & Attfield, J. P. Charge or-

ture

[15] Piekarz, P., Parlinski, K. & Oleś, A. M. Mechanism of

[5] Walz, F. The Verwey transition - a topical review. *J. Phys. Cond. Matter* **14**, R285–R340 (2002).

[6] Khomskii, D. I. *Transition Metal Compounds* (Cambridge Univ. Press, Cambridge, 2014).

[7] Leonov, I., Yarceko, A. N., Antonov, V. N., Korotin, M. A. & Anisimov, V. I. Charge and orbital order in Fe$_3$O$_4$. *Phys. Rev. Lett.* **93**, 146404 (2004).

[8] Yamada, Y. Molecular polarons and valence fluctuations in Fe$_3$O$_4$. *Philos. Mag. B* **42**, 377–385 (1980).

[9] Piekarz, P., Parlinski, K. & Oleś, A. M. Mechanism of the Verwey transition in magnetite. *Phys. Rev. Lett.* **97**, 156402 (2006).

[10] Wright, J. P., Attfield, J. P. & Radaelli, P. G. Long range charge ordering in magnetite below the Verwey transition. *Phys. Rev. Lett.* **87**, 266401 (2001).

[11] Subías, G. et al. Structural distortion, charge modulation and local anisotropies in magnetite below the Verwey transition using resonant X-ray scattering. *J. Synchrotron Rad.* **19**, 159–173 (2012).

[12] Hoesch, M. et al. Anharmonicity due to electron-phonon coupling in magnetite. *Phys. Rev. Lett.* **110**, 207204 (2013).

[13] Bosak, A. et al. Short-range correlations in magnetite above the Verwey temperature. *Phys. Rev. X* **4**, 011040 (2014).

[14] Perversi, G. et al. Co-emergence of magnetic order and structural fluctuations in magnetite. *Nat. Commun.* **10**, 2857 (2019).

[15] Yamauchi, K., Fukushima, T. & Picozzi, S. Ferroelectricity in multiferroic magnet Fe$_2$O$_4$ driven by noncentrosymmetric Fe$^{2+}$/Fe$^{3+}$ charge-ordering: first-principles study. *Phys. Rev. B* **79**, 212404 (2009).

[16] Pimenov, A. et al. Terahertz conductivity at the Verwey transition in magnetite. *Phys. Rev. B* **72**, 035131 (2005).

[17] Gasparov, L. V. et al. Infrared and Raman studies of the Verwey transition in magnetite. *Phys. Rev. B* **62**, 7939 (2000).

[18] McQueeney, R. J. et al. Influence of the Verwey transition on the spin-wave dispersion of magnetite. *J. Appl. Phys.* **97**, 10A902 (2005).

[19] Borroni, S. et al. Mapping the lattice dynamical anomaly of the order parameters across the Verwey transition in magnetite. *New J. Phys.* **19**, 103013 (2017).

[20] Huang, H. Y. et al. Jahn-Teller distortion driven magnetic polarons in magnetite. *Nat. Commun.* **8**, 15929 (2017).

[21] Borroni, S. et al. Light scattering from the critical modes of the Verwey transition in magnetite. *Phys. Rev. B* **98**, 184301 (2018).

[22] Elnaggar, H. et al. Site selective spin and orbital excitations in Fe$_3$O$_4$. Preprint at https://arxiv.org/abs/1811.04836 (2018).

[23] De Jong, S. et al. Speed limit of the insulator-metal transition in magnetite. *Nat. Mater.* **12**, 882–886 (2013).

[24] Randi, F. et al. Phase separation in the nonequilibrium Verwey transition in magnetite. *Phys. Rev. B* **93**, 054305 (2016).

[25] Sammelsen, E. J. & Steinsvoll, O. Low-energy phonons in magnetite. *Phys. Status Solidi B* **61**, 615–620 (1974).

[26] Stevens, T. E., Kuhl, J. & Merlin, R. Coherent phonon generation and the two stimulated Raman tensors. *Phys. Rev. B* **65**, 144304 (2002).

[27] Wall, S. et al. Ultrafast changes in lattice symmetry probed by coherent phonons. *Nat. Commun.* **3**, 721 (2012).

[28] Schaefer, H., Kabanov, V. V. & Densar, J. Collective modes in quasi-one-dimensional charge-density wave systems probed by femtosecond time-resolved optical studies. *Phys. Rev. B* **89**, 045106 (2014).

[29] Yamada, Y., Wakabayashi, N. & Nicklow, R. M. Neutron diffuse scattering in magnetite due to molecular polarons. *Phys. Rev. B* **21**, 4642 (1980).

[30] Borroni, S. et al. Coherent generation of symmetry-forbidden phonons by light-induced electron-phonon interactions in magnetite. *Phys. Rev. B* **96**, 104308 (2017).

[31] Matsumaga, R. et al. Light-induced collective pseudospin precession resonating with Higgs mode in a superconductor. *Science* **345**, 1145–1149 (2014).

[32] Giorgianni, F. et al. Leggett mode controlled by light pulses. *Nat. Phys.* **15**, 341–346 (2019).

[33] Kampfrath, T., Tanaka, K. & Nelson, K. A. Resonant and nonresonant control over matter and light by intense terahertz transients. *Nat. Photon.* **7**, 680–690 (2013).

[34] Duvillaret, L., Garet, F. & Coutaz, J.-L. A reliable method for extraction of material parameters in terahertz time-domain spectroscopy. *IEEE J. Sel. Top. Quantum Electron.* **2**, 739–746 (1996).

[35] Blüchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953 (1994).

[36] Perdew, J. P. et al. Restoring the density-gradient expansion for exchange in solids and surfaces. *Phys. Rev. Lett.* **100**, 136406 (2008).

[37] Kresse, G. & Furthmüller, J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169 (1996).

[38] Liechtenstein, A. I., Anisimov, V. I. & Zaanen, J. Density-functional theory and strong interactions: orbital ordering in Mott-Hubbard insulators. *Phys. Rev. B* **52**, R5467(R) (1995).

[39] Parlinski, K., Li, Z. Q. & Kawazoe, Y. First-principles determination of the soft mode in cubic ZrO$_2$. *Phys. Rev. Lett.* **78**, 4063 (1997).

[40] Parlinski, K. Phonon software, Kraków (2013).

[41] Piekarz, P., Parlinski, K. & Oleś, A. M. Origin of the Verwey transition in magnetite: group theory, electronic structure, and lattice dynamics study. *Phys. Rev. B* **76**, 165124 (2007).

[42] Fukuyama, H. & Lee, P. A. Dynamics of the charge-density wave. I. Impurity pinning in a single chain. *Phys. Rev. B* **17**, 535 (1978).

[43] Lee, P. A. & Rice, T. M. Electric field depinning of charge density waves. *Rev. Mod. Phys.* **50**, 505 (1978).
[54] Harrison, W. A. Electronic Structure and the Properties of Solids: The Physics of the Chemical Bond (W. H. Freeman and Co., San Francisco, 1980).

[55] Takai, S., Akishige, Y., Kawaji, H., Atake, T. & Sawaguchi, E. Low-temperature heat capacities and Verwey transition of magnetite. J. Chem. Thermodyn. 26, 1259–1266 (1994).

[56] Prasankumar, R. P. & Taylor, A. J. Optical Techniques for Solid-State Materials Characterization (CRC Press, Boca Raton, 2012).

[57] Okamoto, H. et al. Photoinduced transition from Mott insulator to metal in the undoped cuprates Nd$_2$CuO$_4$ and La$_2$CuO$_4$. Phys. Rev. B 83, 125102 (2011).

[58] Ascher, E. & Kobayashi, J. Symmetry and phase transitions: the inverse Landau problem. J. Phys. C: Solid State Phys. 10, 1349–1363 (1977).

[59] Hatch, D. M. & Stokes, H. T. Complete listing of order parameters for a crystalline phase transition: a solution to the generalized inverse Landau problem. Phys. Rev. B 65, 014113 (2001).

[60] Aroyo, M. I. et al. Bilbao Crystallographic Server I: databases and crystallographic computing programs. Z. Krist. 221, 15–27 (2006).

[61] Wright, J. P., Attfield, J. P. & Radaelli, P. G. Charge and spin ordering in the nickelates. Phys. Rev. Lett. 85, 214422 (2002).

[62] Lee, S., Chen, R. & Balents, L. Landau theory of charge and spin ordering in the nickelates. Phys. Rev. Lett. 106, 016405 (2011).

[63] Elcoro, L. et al. Double crystallographic groups and their representations on the Bilbao Crystallographic Server. J. Appl. Cryst. 50, 1457–1477 (2017).

[64] Hatch, D. M. & Stokes, H. T. INVARIANT: program for obtaining a list of invariant polynomials of the order-parameter components associated with irreducible representations of a space group. J. Appl. Cryst. 36, 951–952 (2003).

[65] Nazarenko, E. et al. Resonant x-ray diffraction studies on the charge ordering in magnetite. Phys. Rev. Lett. 97, 056403 (2006).

[66] Kukreja, R. et al. Orbital domain dynamics in magnetite below the Verwey transition. Phys. Rev. Lett. 121, 177601 (2018).