Light scattering from the critical modes of the Verwey transition in magnetite

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We present inelastic light scattering data on a single crystal of magnetite (Fe_3O_4) across the Verwey transition. We identify anomalies of the lattice vibrations that originate from strong coupling to electronic excitations. We reveal spectroscopic signatures of diffusive modes in the electronic contribution to the Raman response function. We thereby provide information on the critical dynamics and the hierarchy of the structural and electronic modes in the mechanism of the Verwey transition.

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I. INTRODUCTION

Magnetite (Fe₃O₄) is the best known magnetic material, and it is of great interest from a fundamental point of view. Remarkably, despite extensive studies, the microscopic origin of the physical properties of magnetite is the subject of ongoing debate. At a sample-dependent temperature around 120 K, the interrelation between structural and electronic dynamics causes atomic displacements and the onset of charge and orbital order, the so-called Verwey transition, which has been the focus of experimental and theoretical attention for decades [1]. The Verwey transition impacts both the symmetry of the crystal structure and the electronic ground state. On cooling across the transition temperature, also referred to as the Verwey temperature, T_V , the former is lowered from cubic to monoclinic, whereas the latter changes from conductive to insulating. In the past two decades, accurate diffraction experiments disclosed the most elusive features of the crystal structure and the charge and orbital order in the monoclinic phase [2-5]. In particular, the constitutive units of the sublattice of octahedral Fe ions, or B-type Fe ions, are small polarons (SPs) named trimerons, comprised of an extra electron delocalized over three ions and the atomic displacements of the end ions toward the central ion [4,5]. It was suggested that, in the cubic phase, dynamic fluctuations of trimerons would aggregate into complexes, responsible for the persistence of local electronic and structural correlations for finite times. The thermodynamics of precursor order above the ordering temperature gives rise to a broad ensemble of critical effects [6–12].

The consequences of pretransitional phenomena on the conducting state in the cubic phase are still poorly explored. In general, the transport mechanism and the degree of delocalization of the charge carriers remain under discussion. Optical spectroscopy in the midinfrared has so far been inconclusive as to the possible occurrence of a Drude peak due to the predominance of phonon features in the same frequency range and sensitivity limitations from the Kramers-Kronig analysis of the reflectivity data [13-15]. On the other hand, THz experiments [16] have shown a narrow Drude response ($\sim 40 \text{ cm}^{-1}$) above the Verwey temperature with a small spectral weight $(\sim 2 \times 10^{-4} \text{ of the expected low-energy sum rule})$ compatible with the dc conductivity and suggesting thermally activated heavy carriers. Below the Verwey temperature, a power-law behavior is found for the frequency-dependent conductivity suggesting hopping conduction. The most plausible scenario is that SP conduction dominates both the cubic and monoclinic phases, and the progressive destruction of precursor order and the higher rate of multiphonon processes with increasing temperature govern the competition between regimes of band and hopping conduction [17].

The open problems on the microscopic process of the Verwey transition and the conduction mechanism are mutually related. Indeed, the scenario of a pseudospin-phonon coupled system, first put forth by Yamada, is consistent with the pre-dominance of charge carriers with large effective mass, which mainly give rise to hopping, rather than band, conduction [18]. Conversely, in the framework of a Hubbard-Mott or Peierls transition, electron-phonon coupling is not strong enough for charge carriers to self-trap, with the results that they preserve a high propensity to coherent motion [19,20].

Inelastic light scattering is an effective tool that can be used to gain insight into both lattice-dynamical and electronic effects of phase transitions in solids. Here, we address the previously mentioned intricate puzzle from different perspectives. We take advantage of the broad potentials of Raman spectroscopy in the study of vibrational effects to identify the structural anomalies concomitant with the Verwey transition. At the same time, we provide evidence of contributions to the Raman response from diffusive modes of an electronic nature. Notably, we single out spectroscopic fingerprints from

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FIG. 1. Complete data sets of Raman spectra as a function of nominal temperature for (a) 2.4 and (b) 3.1 eV excitation. Data are normalized to the background intensity integrated between 800 and 810 cm⁻¹. Red (green) arrows indicate magnetite (hematite) phonon modes in the monoclinic phase. Blue-to-red color coding refers to increasing nominal temperature. Black denotes the Verwey temperature.

both charge correlations (characterized by fast dynamics) and diffusive transport, whose characteristic time scales show a critical dependence on temperature.

II. METHODS

The magnetite sample measured in our experiments is a natural single crystal purchased from Surface Preparation Laboratory (SPL), Zaandam, the Netherlands. Based on an ac susceptibility characterization, it presents a discontinuous transition at the Verwey temperature $T_V = 116$ K. The sample was mounted on the cold finger of a liquid-helium cryostat at a base pressure of 10^{-6} mbar. The sample surface was polished to optical quality without any specific orientation of the crystal face.

Raman experiments were conducted in the 5-330 K temperature range by means of a homemade Raman spectrometer equipped with a liquid-nitrogen-cooled CCD detector. In two different sets of experiments, the sample was illuminated by the 514.5 nm output of an argon-ion laser and the 405 nm emission line of a diode laser, with 10 mW nominal power incident onto the sample surface. In the following, the two different excitations are denoted by their photon energies, $h\nu = 2.4$ and 3.1 eV, respectively. Raman spectra were acquired in an unpolarized backscattering configuration. Due to the experimental limitations in the rejection of the Rayleigh light, the lower boundaries of our detection ranges are 75 and 140 cm⁻¹, respectively, for 2.4 and 3.1 eV excitation. As a result of the large effects of laser heating, for 2.4 eV excitation the Verwey transition occurs at a nominal temperature $T_V^* = 85$ K. Asterisks in superscripts denote reference to the nominal temperature for 2.4 eV excitation. To compensate for the difference in the nominal temperatures, combined data are plotted as a function of the reduced temperature,

defined as $T^*/T_V^* - 1$ and $T/T_V - 1$, respectively, for 2.4 and 3.1 eV excitation. Accordingly, our approximate estimate of the effective temperature at the laser spot for 2.4 eV excitation is $T = T^* T_V/T_V^*$. Data sets in the full temperature range of our experiments are shown in Fig. 1.

III. RESULTS AND DISCUSSION

As illustrated in Fig. 2, in our study we take into account three possible contributions to the Raman spectra, namely scattering of light by phonons, magnons, and electrons, with propagating or diffusive dynamics. Typically, the first two types of collective excitations produce narrow and broad peaks, respectively, superimposed to an intensity continuum from electronic Raman scattering. In a phenomenological description, the total Raman response, $S(\omega)$, can be fit by the sum of three separate components, $S_{ph}(\omega)$, $S_{ma}(\omega)$, and $S_{el}(\omega)$, associated with lattice vibrational, magnetic, and electronic degrees of freedom, respectively. According to the



FIG. 2. Pictorial representation of the different contributions to the Raman response function of magnetite from phonons, magnons, and electrons, with diffusive or propagating dynamics.



FIG. 3. Spectral response obtained for 2.4 eV excitation at (a) 293 and (b) 5 K, and for 3.1 eV excitation at the same reduced temperatures. Red (green) arrows indicate magnetite (hematite) phonon modes. Labels in red refer to the cubic counterparts of the phonon modes in the monoclinic phase. For better comparison, data are normalized to the background intensity integrated between 800 and 810 cm⁻¹.

fluctuation-dissipation theorem, the scattering cross section in Raman experiments, $S(\omega)$, is proportional to the imaginary part of the Raman response function, $\chi''(\omega)$,

$$S(\omega) = [1 + n(\omega)]R \chi''(\omega), \qquad (1)$$

where $1 + n(\omega) = [1 - \exp(-\omega/k_B T)]^{-1}$ is the Bose-Einstein thermal factor. Matrix element effects are incorporated in the proportionality factor *R*. To a first approximation, it can be assumed to be temperature- and frequencyindependent. In the following, Raman spectra corrected by the Bose factor, $R \chi''(\omega)$, are accounted for. For simplicity, they are referred to as the spectral response.

A. Phonon excitations

First, we focus on the contribution to the spectral response from the phonon modes with Raman activity, generally modeled by Lorentzian functions, with frequency ω_i , linewidth Γ_i , and amplitude A_i ,

$$S_{\rm ph}(\omega) = [1+n(\omega)] \sum_{i=1}^{N} \frac{A_i \omega \Gamma_i}{\left(\omega^2 - \omega_i^2\right)^2 + \omega^2 \Gamma_i^2}.$$
 (2)

The crystal structure of magnetite above T_V is an inverse cubic spinel with space group $Fd\bar{3}m$. According to factorgroup analysis, the space group $Fd\bar{3}m$ is decomposed into irreducible representations, which are further grouped into $(T_{1g} + 2A_{2u} + 2E_u + 2T_{2u})$ inactive modes, $(A_{1g} + E_g + 3T_{2g})$ Raman-active modes, and $(5T_{1u})$ infrared-active modes. Raman- and infrared-active modes are mutually exclusive for the presence of inversion symmetry.

Verble first analyzed the eigenvectors of the five Ramanactive modes of the cubic phase with reference to Waldron's molecular model [21,22]. Based on symmetry considerations, only tetrahedral Fe³⁺ ions and O²⁻ ions contribute to Ramanactive modes. In particular, according to Verble's description, they comprise symmetric stretching of O²⁻ ions along Fe³⁺–O²⁻ bonds (A_{1g} mode), symmetric and asymmetric O–Fe–O bending (E_g and T_{2g}^2 modes, respectively), asymmetric stretching of Fe³⁺ and O²⁻ ions (T_{2g}^3 mode), and rigid displacements in opposite directions of the two Fe³⁺O₄²⁻ tetrahedra in the primitive cell (T_{2g}^1 mode, the numbering of the T_{2g} modes, different from Verble's, is the same as Ref. [23]). The validity of Waldron's molecular model depends on the relative importance of the interactions within and among *B*-type Fe tetrahedra and Fe³⁺O₄²⁻ tetrahedra. Combined theoretical and experimental studies of the phonon density of states suggest comparable contributions to the overall structural dynamics from both tetrahedral and octahedral Fe ions below 320 cm⁻¹ [24,25]. On the other hand, first-principles computations of the eigenvectors of the Ramanactive modes under consideration are in qualitative agreement with Verble's description [26].

As displayed in Fig. 3(a), in our spectral responses at room temperature, four out of the five Raman-active modes predicted by group theory are observable. The same figure summarizes our mode assignment, which relies on polarized Raman studies by Shebanova and Lazor, with particular reference to the controversial attribution of the 307 cm⁻¹ peak to the E_g or T_{2g}^3 mode [23]. Let us note that Shebanova and Lazor's assignment is also supported by ab initio calculations of the phonon-dispersion curves in the cubic phase, in quantitative agreement with the experimental data [26,27]. The additional peaks at 291 and 412 cm⁻¹ were identified with the $E_g^2 + E_g^3$ and E_g^4 hematite modes, respectively [28]. Our fit analysis allowed us to discriminate the E_g modes of hematite and magnetite, which are close in energy and give rise to a broad asymmetric band from 280 to 340 cm⁻¹ [see Figs. 7(a) and 7(b)]. The presence of hematite impurities is not surprising considering the natural origin of our sample.

In the structural transition of magnetite, complex atomic displacements, with small amplitudes down to 1 pm, give rise to a change in crystal symmetry, which is reflected in the modifications of a number of physical properties [2–5]. A monoclinic cell four times larger than the cubic cell accounts for the complete set of structural distortions that take place upon decreasing the temperature from above to below T_V . As a direct consequence, the number of normal modes of vibration also quadruplicates, from 42 to 168. Therefore, as illustrated in Fig. 3(b), the phase transition is accompanied by the emergence of a rich spectrum of new phonon modes. For a complete assignment of the Raman-active modes in the monoclinic phase, first-principles computations that can reproduce mode frequencies and Raman cross sections with quantitative



FIG. 4. (a) Temperature dependence of the intensity of the critical modes for 3.1 eV excitation. Reference data for the A_{1g} mode are also plotted. Temperature dependence of the (b) area and (c) center of gravity of the background distribution in the 240–500 cm⁻¹ Raman shift range. Violet (green) symbols refer to 3.1 eV (2.4 eV) excitation. Lines are guides to the eye. Vertical dashed lines denote the Verwey temperature.

accuracy are needed. For our purposes, we restrict ourselves to simpler considerations. The highest-frequency mode is the monoclinic counterpart of the A_{1g} mode in the cubic phase, now labeled A_g . The linewidths of the T_{2g} modes increase, instead of decreasing for anharmonic effects, upon lowering the temperature in the pretransition region [see Figs. 5(d) and 5(f)]. This is interpreted here as the result of mode splitting into submodes close in energy. Its occurrence tens of degrees Kelvin above T_V , rather than at T_V , is among the precursor effects discussed at the end of Sec. III B. No further consideration is possible here on the relation between the shoulder mode around 628 cm⁻¹ and the A_{1g} mode, as well as between the two new modes in the 300–400 cm⁻¹ frequency range and the E_g mode, which thus remain unassigned.

Two sharp peaks unrelated to any Raman-active mode of the cubic phase appear around 160 and 470 cm⁻¹, consistent with previous observations on magnetite thin films [29]. In recent pump-probe studies, based on the comparison between experimental data and theoretical computations of the phonon-dispersion curves and the optical functions, we attributed the onset of the 160 cm⁻¹ peak to the folding to the center of the Brillouin zone of a phonon mode of Δ_2 symmetry at $q_{\Delta} = (0, 0, 0.5)$ reciprocal-lattice units (r.l.u., 1 r.l.u. $= 2\pi/a$, with a the lattice parameter in the cubic phase) [30]. With the use of the same method, we assigned an additional mode at 125 cm⁻¹ to the monoclinic counterpart of a phonon mode of X_3 symmetry at the boundary of the Brillouin zone in the [001] direction. The latter mode is visible as a broad weak peak in our data at 5 K and 2.4 eV excitation [see Fig. 1(a)], and is not discussed any further.

In early Raman experiments, the 470 cm⁻¹ band was observed at 130 and 300 K, and it was proposed to originate from an optical magnon [31–33]. Indeed, the band position is compatible with energy estimates for the lowest-energy optical magnon of the cubic phase from inelastic neutron scattering (INS) [34]. However, in more recent experiments, the 470 cm⁻¹ band was not observed at high temperatures [15,23,29,35–37]. In particular, in our measurements the temperature dependence of the band intensity is consistent with that of a phonon mode of the monoclinic phase. The intensity decreases rapidly across the Verwey transition, but residual intensity persists in the cubic phase for the precursor effects discussed in the next subsection [see Fig. 4(a)]. Conversely, if an optical magnon of the cubic phase was the cause of the band under consideration, the intensity would decrease upon heating, but no complete band suppression would take place far above T_V . The observation of the 470 cm⁻¹ band at 300 K in Refs. [31,33] is hardly explainable by invoking precursor effects. An alternative suggestion is that the peak observed at room temperature is in fact a different phonon mode of the cubic phase, namely the T_{2g}^3 mode predicted in the same energy range based on theoretical computations [23,26,27]. Sample-dependent effects may play a role in its intensity enhancement [31–33].

B. Structural anomalies

Figures 5 and 6 illustrate the temperature dependence of the frequencies and linewidths of the phonon modes across the Verwey transition. In our experiments, small temperature steps down to 5 K were used in order to best resolve the possible occurrence of structural anomalies by means of a quantitative analysis. The single peaks associated with the phonon modes were fit with Lorentzian functions according to Eq. (2), after subtraction of a linear baseline in the Raman shift range around the peak. The fit analysis of the features in between 240 and 440 cm^{-1} required a different method, briefly described in Sec. III C. Modifications in mode parameters are rapid for all modes. A large frequency decrease and a linewidth increase by, respectively, 5-10 and 3-6 cm⁻¹ take place in proximity of the Verwey transition. Inhomogeneous laser heating broadens the critical region and thus causes a rounding of the temperature dependence of the mode parameters on the lower-temperature side. Instead, the steep decrease in the mode frequency between T_V and $T_V + 14$ K is an intrinsic effect. The onset of linewidth broadening, about 40 K



FIG. 5. Temperature dependence of the frequency and linewidth of the (a,b) A_{1g} , (c,d) T_{2g}^2 , and (e,f) T_{2g}^1 modes of the cubic phase, visible in the form of single peaks both above and below T_V . Violet (green) symbols refer to 3.1 eV (2.4 eV) excitation. A vertical dashed line denotes the Verwey temperature. The lower horizontal axis is the nominal temperature for 3.1 eV excitation and our approximate estimate of the effective temperature at the laser spot for 2.4 eV excitation.

below T_V , precedes the decrease in the mode frequencies, starting from 95 K.

Our data provide unequivocal evidence of the concurrent lattice dynamical and electronic character of the Verwey transition. According to the most recent theoretical and experimental estimates, charge differences between Fe ions in the insulating state are on the order of one-tenth of an elementary charge [4,5,38]. This explains why the occurrence itself of charge order has long remained controversial [39,40]. However, the occupations of different 3d orbitals at B-type Fe ions constitute an unambiguous basis upon which to define order parameters (OPs). Orbital, rather than charge, order was suggested to play the most important role in the modifications of the electronic structure from the conducting to the insulating state [27]. The important renormalization of the mode frequencies observed here despite the small amplitude of the atomic displacements is a direct consequence of the onset of orbital polarization below the transition temperature. Moreover, the comparable values of the frequency changes support a cooperative picture of the Verwey transition. According to this scenario, no significant hierarchy is established among the phonon modes, since they all participate in the transformation process, although with measurable differences in their contributions, particularly in terms of coupling with different types of modes.

In this regard, the temperature dependences of both the 160 and 470 cm⁻¹ modes resemble phonon softening, but

only partially [see Figs. 6(c) and 6(e)]. This is different from the general behavior of the phonon modes, including the 628 cm⁻¹ mode and those close to the E_g mode, which are also intrinsic to the monoclinic phase alone. None of them exhibits any important change in frequency over the temperature range below 95 K [see the upper panels of Figs. 5 and 6(a)]. Figures 7(c) and 7(d) show the temperature dependence of the line shapes of the 160 and 470 cm⁻¹ modes to the highest temperatures at which they are visible. The distribution of scattering intensity from the two modes and the temperature range over which they contribute to Raman scattering are anomalous. In both cases, particularly close to the transition temperature, the best fit quality is obtained with Fano, rather than Lorentzian, functions. Unlike Lorentzian peak shapes, the two modes are asymmetric and, in particular, the spectral weight is larger on the low-frequency side. Close to the transition temperature, a dip develops on the highfrequency side, in further agreement with a Fano line shape. To gain reliable information on the temperature dependence of the line-shape anomaly, the two peaks are also fit with bi-Gaussian functions. Fano functions correctly reproduce the peaks within the local frequency range, however the accuracy of the fit parameters depends on the quality of the background subtraction over a broad frequency range. To quantify the degree of asymmetry, an asymmetry parameter is defined, $\beta \equiv$ $(\Gamma_1 - \Gamma_2)(\Gamma_1 + \Gamma_2)^{-1}$, where Γ_1 and Γ_2 are, respectively, the left and right half-widths at half-maximum from the fit



FIG. 6. Temperature dependence of the frequency and linewidth of Raman-active modes of the monoclinic phase. Violet (green) symbols refer to 3.1 eV (2.4 eV) excitation. The shoulder mode of the A_{1g} mode in panels (a) and (b) is clearly observable only for 3.1 eV excitation. A vertical dashed line denotes the Verwey temperature. The lower horizontal axis is the nominal temperature for 3.1 eV excitation and our approximate estimate of the effective temperature at the laser spot for 2.4 eV excitation.

with bi-Gaussian functions. The asymmetry parameter of the 470 cm⁻¹ mode does not present any meaningful dependence on temperature throughout the monoclinic phase. Instead, it suddenly diverges in the proximity of the critical region. The degree of asymmetry does not change for different excitations. In particular, $\beta = 0.27 \pm 0.03$ and 0.29 ± 0.06 , respectively, for 3.1 and 2.4 eV excitation. The degree of asymmetry of the 160 cm⁻¹ mode is lower than that of the 470 cm⁻¹ mode and does not depend on excitation energy either, namely $\beta = 0.16 \pm 0.15$ and 0.18 ± 0.11 , respectively, for 3.1 and 2.4 eV excitation.

Recent pump-probe studies revealed that two modes that are symmetry-forbidden in the cubic phase but symmetryallowed in the monoclinic phase, namely the 125 and 160 cm⁻¹ modes, persist up to T_V + 24 K [30]. Assuming that such experiments probe in real time the same Raman tensor that governs the present steady-state experiments [41], one would expect the analogous effect to be observed here. Unfortunately, artifacts from ineffective rejection of the Rayleigh light in the low-frequency range prevent any conclusion on whether the 160 cm⁻¹ mode is visible also in our steady-state experiments for the same 3.1 eV photon energy of light excitation. On the other hand, we observe some analogous effect for other modes. The intensity of the 470 cm⁻¹ mode does decrease suddenly around T_V , however a broad weak feature is observable up to 120–125 K nominal temperature, which corresponds to an effective temperature more than 5–10 K above the transition temperature [see Fig. 7(c)]. Analogous considerations hold true for the shoulder mode of the A_{1g} mode [see Figs. 1(b) and 4(a)]. A reliable fit analysis of the A_{1g} and T_{2g}^2 modes requires an additional peak in the 600–650 cm⁻¹ Raman shift range up to 150 K nominal temperature. However, the superposition of the spectral weight associated with the A_{1g} peak does not allow us to study possible anomalies in line shape.

To explain this effect, we refer to the same interpretation as in Ref. [30]. In the high-symmetry phase, the modes are nominally forbidden simply because they are at finite wave vector. However, fluctuations of the ordered phase with a large correlation length and time can explain the effect. Indeed, we propose that a second-order Raman process takes place in which a charge fluctuation with wave vector q close to that of the ordered phase is excited together with a phonon mode of wave vector -q, so that the total wave vector is conserved. The cross section for the above Raman mechanism is meaningful only for large amplitude and a high enough degree of correlation of the critical fluctuations, near the Verwey temperature. The diffusive character of the electronic modes explains why they do not contribute any energy.

Notice that the Fano line shapes observed for the critical modes point to interference effects between scattering of light by phonon modes and a continuous spectrum of electronic



FIG. 7. Temperature dependence of phonon modes and background intensity in the 240–500 cm⁻¹ Raman shift range for (a) 2.4 and (b) 3.1 eV excitation. Red (green) arrows indicate magnetite (hematite) phonon modes. A blue arrow denotes the central energy of the higherenergy acoustic magnon at the Δ point at 115 K < T_V from INS [42]. Data are offset for clarity. Temperature dependence of the monoclinic modes at (c) 470 and (d) 160 cm⁻¹ for 3.1 eV excitation. Red (blue) refers to the cubic (monoclinic) phase. For better comparison, data are normalized to the background intensity integrated between 800 and 810 cm⁻¹. For clarity, data are offset and multiplied by a factor 5 close to the Verwey temperature. Data and fitting functions are plotted with colored symbols and lines, respectively. Black lines represent separate fit components.

excitations and, therefore, to significant electron-phonon coupling for the lattice vibrations under consideration.

C. Magnetic or electronic excitations

As illustrated in Fig. 1, intensity builds up in the monoclinic phase in the form of a broad background in the Raman shift range from 240 to 500 cm⁻¹. Gasparov *et al.* suggested a possible electronic or magnetic origin of this feature, rather than the simple onset of a rich structure of new phonon modes [36]. In our fit analysis in Figs. 7(a) and 7(b), baseline estimation via an asymmetric least-squares method singles out the phonon modes from the background. It is thereby possible to study the temperature dependence of the background. The integrated intensity of the background decreases rapidly with increasing temperature across the Verwey transition [see Fig. 4(b)]. The center of gravity of the baseline does not change noticeably throughout the monoclinic phase, and it is about 362 ± 2 and 368 ± 3 cm⁻¹, respectively, for 2.4 and 3.1 eV excitation [see Fig. 4(c)].

INS measurements of the spin-wave dispersion of magnetite below T_V revealed the formation of a large gap in the acoustic branch at q_{Δ} . The modifications of the spin-wave and phonon dispersions of magnetite upon the Verwey transition are qualitatively analogous. Indeed, the sizes of the magnetic moments and the exchange constants depend significantly on the charge distribution and the bond lengths and angles, all of which change discontinuously upon the ordering process of the Verwey transition [42]. Upon decreasing temperature across T_V , the volume of the primitive cell quadruplicates, both for the magnetic and electronic structures. In reciprocal

space, q_{Δ} becomes the center of the Brillouin zone. Close to both edges of the gap, the spin-wave dispersions become flat and thus give rise to a high magnon density of states, along with a potential contribution to the optical and Raman responses [42].

The center of gravity of the background distribution is close to the 375 cm^{-1} frequency estimate of the higherenergy magnon at the gap from the same INS experiments at 115 K $< T_V$ [see the blue arrows in Figs. 7(a) and 7(b)] [42]. However, it is arguable whether a one-magnon excitation is responsible for the broad peak observable in our Raman spectra. According to the microscopic theory by Fleury and Loudon, the same mechanism is responsible for first-order scattering in all types of magnetic materials, namely indirect electric-dipole coupling, mediated by spin-orbit interaction [43,44]. The selection rule on the ϵ_1 and ϵ_2 polarizations of, respectively, incoming and outgoing light is $|\epsilon_1^z \epsilon_2^+ - \epsilon_1^+ \epsilon_2^z| \neq$ 0, where $\epsilon^+ = \epsilon^x + i\epsilon^y$ and z is the direction of spin order. Therefore, in polarized Raman studies, Raman scattering from one-magnon excitations is supposed to disappear if ϵ_1 and ϵ_2 are parallel. This is not the case for the broad peak being considered, which is also observable in XX geometry [15,36]. Its large linewidth further calls into question its possible origin from a one-magnon excitation. In fact, first-order scattering is restricted to the center of the Brillouin zone and is thus supposed to give rise to narrow peaks.

An alternative suggestion is the occurrence of second-order scattering from magnon excitations of opposite wave vectors close to the boundaries of the Brillouin zone in the monoclinic phase at $(0, 0, \pm 0.25)$ r.l.u.. Energy conservation is fulfilled because they are at about half the energy of the magnon



FIG. 8. Comparison between the spectral response, $R \chi''(\omega)$ (black), at the transition temperature and in the (a) (blue) monoclinic and (b) (red) cubic phase. The fitting functions to the background intensity defined in Eq. (3) are plotted together with the data, with the same color coding. Shaded areas highlight the diffusive contribution to the spectral response. (c)–(e) (black symbols): Temperature dependence of the fit parameters. The reduced temperature dependence of the dc conductivity of our sample is also plotted with a red line in panel (d). The lower horizontal axis of panels (c)–(e) is the nominal temperature. Vertical dashed lines denote T_V^* . To account for the effects of laser heating, fits are repeated for $R \chi''(\omega)$ computed from $S(\omega)$, respectively, with reference to our estimate of the effective temperature, T, and the nominal temperature, T^* . Error bars correspond to the differences between the fit parameters in the above two cases. Data points are average values.

excitations at q_{Δ} [42]. In contrast to first-order processes, second-order processes take place via different mechanisms depending on the type of magnetic material [43,44]. The so-called exchange scattering mechanism is characterized by the absence of intrinsic selection rules on ϵ_1 and ϵ_2 , i.e., both symmetric and antisymmetric components of the Raman tensor. Moreover, typical cross sections are comparable to or larger than those for one-magnon scattering, and the multiple combinations of magnon excitations possible around the critical points of the Brillouin zone produce broad peaks, similar to our observations. However, available data from INS experiments do not show any noticeable gap at $(0, 0, \pm 0.25)$ r.l.u. [42]. A small gap may still be present. To determine whether Van Hove singularities develop at $(0, 0, \pm 0.25)$ r.l.u., data with better energy and momentum resolution are needed.

An electronic origin of the feature being discussed is also possible. The onset of charge and orbital order, and the different electronic structure in the monoclinic phase, compared to the cubic phase, may indeed produce rearrangements of the spectral weight in the Raman response. However, before any further speculation, additional Raman experiments are needed to rule out magnon excitations altogether, for instance high magnetic field and polarization dependences on an oriented single crystal in the monoclinic phase.

D. Diffusive excitations

In our discussion of the diffusive response, we take into account data at 2.4 eV excitation, which, in contrast to data at 3.1 eV excitation, are available on a spectral range suitable for an analysis down to low frequency. Interestingly, an anomaly in the background intensity occurs at low frequency in the critical region. First, in the monoclinic phase, the background intensity increases upon heating. Then, in the cubic phase, an atypical transfer of spectral weight to higher frequency takes place upon further increasing the temperature. Accordingly, in Figs. 8(a) and 8(b), the background intensity at low frequency is below that of reference data at T_V both in the monoclinic and cubic phases.

The following function represents the simplest model to fit the background intensity in our data, with particular reference to the low-frequency range,

$$R \chi_{\rm el}''(\omega) = \frac{A\omega}{1 + (\omega\tau)^2},\tag{3}$$

where A is a phenomenological amplitude and τ is a phenomenological time constant. Our fit analysis is exemplified in Figs. 8(a) and 8(b). Data sets and fitting functions at different temperatures throughout both the cubic and monoclinic phase are shown in Fig. 1 of the Supplemental Material [45]. The fitting parameters A and τ are plotted as a function of temperature in Figs. 8(c) and 8(d). It has been shown that, to a first approximation, the simple relation $R \chi_{el}^{\prime\prime}(\omega) \propto \omega \sigma_1(\omega)$ holds true between the electronic contribution to the spectral response, $\chi_{el}^{\prime\prime}(\omega)$, and the real part of the optical conductivity, $\sigma_1(\omega)$, at low enough frequency [46]. Therefore, it is possible that our data contain the Drude peak, which originates from the diffusive dynamics of the charge carriers. If this is the case, the phenomenological amplitude A is supposed to account for the contribution to $\sigma_1(0)$ from the transport mechanism under consideration, $A \propto \sigma_1(0) = ne^2 \tau m^{*-1}$, where *n* and m^* are, respectively, the density and effective mass of the charge carriers. Indeed, as shown in Fig. 8(d), the temperature dependences of A and $\sigma_1(0)$ are qualitatively similar in the cubic phase. Our estimate of the ratio between the density and the effective mass of the charge carriers, $n/m^* \propto A/\tau$, shown in Fig. 8(e), increases continuously upon heating, which is suggestive of thermally activated processes. Our data do not allow us any further consideration on the nature of the transport mechanism being discussed. Ihle and Lorenz proposed a microscopic theory for SP conduction in magnetite, according to which diagonal transitions give rise to a Drude peak in $\sigma_1(\omega)$, which dominates $\sigma_1(0)$ below 400 K [17]. However, their considerations are called into question by the erroneous assignment of the polaron peak [14].

The interpretation of the Raman diffusive excitation as being related to the Drude response in the optical conductivity is incompatible with the order of magnitude larger scattering time observed in THz experiment [16] and with the insulating character of the transport below T_V . Furthermore, a Drude interpretation cannot explain the temperature dependence of the relaxation time, τ , plotted in Fig. 8(c) either. In principle, one can argue that, due to a critical slowing down, the relaxation time due to scattering with critical fluctuations increases close to the transition temperature. However, the scattering of the charge carriers by fluctuations of the OP is by no means the only relaxation channel. Phonons, magnons, and different types of fluctuations are also at play. According to Matthiessen's rule, in the presence of competing processes, τ is in any case dominated by the shortest relaxation time. Any possible increase of the time constant in one of the relaxation channels is cut off by the higher scattering rate from different mechanisms.

One can still think that some q = 0 relaxation of charge contributes to Raman but not to the transport due to selection rules. However, it is difficult to conceive how such selection rules would be implemented for an incoherent relaxation process.

Instead, we propose that the observed anomaly in the background intensity comes from a process in which two charge fluctuations with finite momentum are created. The coupling with light does not occur through a correction of the q = 0 charge fluctuation but through a Raman matrix element that directly couples light to a two-mode excitation. Thus, the process is Raman-allowed but does not contribute to the q = 0

current fluctuations that determine the optical conductivity. The two modes are postulated to be critical modes of the Verwey transition. In particular, in the following, we argue that diffusive collective excitations of charge fluctuations provide a scattering channel for the electronic spectral response, in addition to the processes of single-particle excitations. A similar explanation was advanced for Raman scattering in cuprates [47]. Also, this mechanism is closely related to our explanation of the appearance of symmetry-forbidden phonons above the ordering temperature.

A generic fluctuation mode of wave vector q, $\delta \rho_q(t)$, is defined as the instantaneous deviation of the Fourier transform (FT) of an ordering field mode, $\rho_q(t)$, from its equilibrium value, $\langle \rho_q \rangle$, also termed an order parameter (OP), i.e., $\delta \rho_q(t) = \rho_q(t) - \langle \rho_q \rangle$. Above the ordering temperature, which in our case is T_V , $\langle \rho_q \rangle = 0$ by definition, and $\delta \rho_q(t)$ and $\rho_q(t)$ are equivalent. Instead, below the ordering temperature, $\langle \rho_q \rangle \neq 0$ at the critical wave vectors, which we generically indicate as $\{q_c\}$.

The ordering field modes accounted for here are represented by electron density modulations. The fluctuation modes are treated here as classical variables with relaxational responses, consistent with our observation of a diffusive response, along with a general interpretation of the Verwey transition in terms of an order-disorder transformation. We suppose that quantum tunneling of charges does not occur, since charges are self-trapped due to polaronic effects. Still, the treatment is not purely classical, because we do not assume that k_BT is much higher than the energy scale of the ordering field modes.

To compute the diffusive response, we start from the Ginzburg-Landau expansion of the free energy density in reciprocal space, given by Eq. (4). In principle, this formalism is suitable only for second-order transitions. Nevertheless, we apply it to the Verwey transition, with the following caveats. First, the ordering temperature, T_V , must be replaced by the theoretical limit of metastability for the disordered phase, $T_c < T_V$. Second, the critical wave vectors for the discontinuous transition, $\{q_c\}$, commensurate, must be replaced by the critical wave vectors for the continuous precursor effects, $\{q_c^*\}$, incommensurate, where diffuse scattering is the most intense far enough from T_V [7–10,48]. The sums over q in Eq. (4) are restricted to neighborhoods of $\{q_c^*\}$,

$$\mathcal{F}(\{\rho_{q}(t)\}) = \sum_{\boldsymbol{q}_{c}^{*}} \sum_{\boldsymbol{q}} \frac{1}{2} [a(T - T_{c}) + b|\boldsymbol{q} - \boldsymbol{q}_{c}^{*}|^{2}] \rho_{q}(t) \rho_{-q}(t) + \sum_{\boldsymbol{q}_{c}^{*}} \sum_{\boldsymbol{q}} f_{q}(t) \rho_{-q}(t) + o(\rho^{3}).$$
(4)

Below T_V , a similar development holds true, to a reasonable approximation, yet around the finite values of $\langle \phi_q \rangle$. Terms of higher order implicit in $o(\phi^3)$ are responsible for the discontinuous transformation at T_V . *a* and *b* are temperature-independent coefficients. An external field $f_q(t)$ linearly coupled to the ordering field is introduced here for the computation of the diffusive propagator. The details of our calculations are provided in the Appendix. According to our theoretical model, the contribution of the fluctuation modes to the spectral response is given by Eq. (5). We defined



FIG. 9. Comparison between the spectral response, $R\chi''(\omega)$ (black), at the transition temperature and in the (a) (blue) monoclinic and (b) (red) cubic phase. The fitting functions to the background intensity defined in Eq. (5) are plotted together with the data, with the same color coding. Shaded areas highlight the electronic contribution to the spectral response. (c) Our data from spontaneous Raman scattering (SRS, green symbols and shaded area) are compared with data from INS (black symbols and shaded area) [7]. The black line is the theoretical prediction for the correlation time of polaron fluctuations of Δ_5 symmetry at (0,0,0.75) r.l.u. based on experimental estimates of the microscopic parameters of Yamada's model [49]. The lower horizontal axis of panel (c) is the nominal temperature. Vertical dashed lines denote T_V . As in Figs. 8(c)–8(e), data points and error bars account for the uncertainty from the effects of laser heating.

 $m = \gamma a(T - T_c)$, with γ a phenomenological relaxation rate [see Eq. (A1)]. $\omega_M = \gamma b q_M^2$ is the frequency cutoff associated with the upper limit of the summation over the fluctuation modes in reciprocal space, q_M , large enough to contain the fluctuation modes that contribute the most to the spectral response, and of the order of π/a ,

$$R \chi''(\omega) = -\int_{-\infty}^{+\infty} d\xi \frac{1}{\omega\xi} \left[\frac{1}{e^{(\xi+\omega/2)/k_BT} - 1} - \frac{1}{e^{(\xi-\omega/2)/k_BT} - 1} \right] \times \left\{ \left(\xi + \frac{\omega}{2}\right) \left[\arctan\left(\frac{m+\omega_M}{\xi-\omega/2}\right) - \arctan\left(\frac{m}{\xi-\omega/2}\right) \right] - \left(\xi - \frac{\omega}{2}\right) \left[\arctan\left(\frac{m+\omega_M}{\xi+\omega/2}\right) - \arctan\left(\frac{m}{\xi+\omega/2}\right) \right] \right\}.$$
(5)

To understand the meaning of the parameter m, let us consider a simple analogy to experimental techniques with wave-vector resolution, and selective sensitivity to charge and orbital order, such as resonant inelastic x-ray scattering (RIXS) at suitable absorption edges and reflections. Starting from the transport equation for the free-energy density [see Eq. (A1)], it is easy to compute the imaginary part of the dynamical susceptibility at the wave vector \boldsymbol{q} , $\chi''(\boldsymbol{q}, \omega)$, defined as the change in the fluctuation mode at the same point in reciprocal space, consequent to an external field,

$$\chi''(\boldsymbol{q},\omega) = \operatorname{Im}\left[\frac{\rho_{\boldsymbol{q}}(\omega)}{f_{\boldsymbol{q}}(\omega)}\right] = \frac{\gamma\omega}{\omega^2 + (\Gamma/2)^2},\tag{6}$$

with $\Gamma/2 = m + \gamma b |\boldsymbol{q} - \boldsymbol{q}_c^*|^2$. The scattering intensity calculated from the above response function according to the fluctuation-dissipation theorem [see Eq. (1)] is a central peak, i.e., a peak centered at zero energy, of linewidth Γ . This originates from the relaxational dynamics of electronic excitations with correlation time proportional to $1/\Gamma$. Indeed, the scattering intensity is given by the FT of the time autocorrelation of the observable under consideration, in our case the electronic degree of freedom.

Under our assumption of a Ginzburg-Landau functional, the linewidth increases quadratically around the critical wave vector. Therefore, the parameter *m* represents the minimum linewidth, proportional to the maximum inverse correlation time, corresponding to the critical wave vector. Deviations from our theoretical model, for instance the variable degree of instability at different wave vectors, give rise to complications. In the following, $\tilde{\tau} \propto 1/m$ will be generically referred to as the correlation time of the fluctuation modes.

As exemplified in Figs. 9(a) and 9(b), the theoretical model defined in Eq. (5) is fit to our data. By comparison with Figs. 8(a) and 8(b), one can observe that both Eqs. (3) and (5) give a similar quality of fit. Extended data sets and fitting functions are shown in Fig. 2 of the Supplemental Material [45]. A first fit analysis is carried out with independent values of the parameter ω_M . Then, in a second step, the theoretical model is fit again to our data, with parameter ω_M constrained to an identical value, equal to the mean from the first step. Our estimate of the correlation time is plotted against temperature in Fig. 9(c). Above 150 K nominal temperature, equivalent to 0.76 reduced temperature, the correlation time does not show any large change as a function of temperature, and it decreases continuously at a rate of -1 fs/K. Instead, near the transition temperature, the temperature dependence of the correlation time displays a cusplike shape. A more noticeable divergence also sets in upon approaching the lowest temperature.

Any possible conclusion on the temperature dependence of the correlation time in the cubic phase is questioned by the superposition of the contribution from the processes of single-particle excitations discussed earlier. More reliable considerations are feasible close to, or below, T_V , where this is expected to be negligible. An important question is, what is the true nature of the ordering field modes in our observations? Are they indeed electron density modulations, or in fact do they also involve atomic displacements? To address this issue, let us compare our 0.4–0.8 ps estimate of the correlation time around the critical region, down to the onset for the divergence at the lowest temperature, to analogous estimates from INS.

Diffuse scattering of neutrons and nonresonant x rays was observed above T_V [7–10]. In analogy to our observations, it originates from fluctuation modes. In contrast to Raman scattering, in INS and nonresonant inelastic x-ray scattering (NRIXS), the wave-vector transfer is also resolved, and the direct observables are structural instead of electronic. The more intense the diffuse scattering is at a given wave vector, the longer is the correlation time of the fluctuation mode at the same point in reciprocal space. Relative maxima in intensity of diffuse scattering are located at critical wave vectors, i.e., corresponding to the fluctuation modes that manifest the highest instability. In the case of magnetite, above T_V , the critical dynamics is governed by intrinsic instabilities in the liquid of SPs, at incommensurate points in reciprocal space, such as (0,0,0.75) r.l.u. [7]. The black line and symbols plotted in Fig. 9(c) are, respectively, theoretical predictions and experimental estimates of the correlation time of the fluctuation mode of Δ_5 symmetry at (0,0,0.75) r.l.u. from the linewidths of the central peaks in INS [7,49].

The above time scale on the order of picoseconds and the absence of phonon softening are both consistent with the scenario of combined electronic and structural fluctuations, with slow dynamics, compared to the phonon modes. Instead, interestingly, the 0.4–0.8 ps time scale of the ordering field modes in our observations in the temperature range for reliable estimates [see the green shaded area in Fig. 9(c)] suggests a smaller effective mass, compatible with excitations of mainly electronic character.

IV. CONCLUSIONS

In summary, in our study we disentangled the different contributions to light scattering in magnetite from structural, magnetic, and electronic degrees of freedom. We thereby gained important information on the critical modes of the Verwey transition. We suggested a possible magnetic or electronic origin of light scattering in the 240-500 cm⁻¹ range, as a consequence of modifications in the spin-wave dispersions and electronic structure of magnetite upon the Verwey transition. In general, our results are consistent with the concerted contribution of different modes to the essential mechanism of the Verwey transition. Nonetheless, from a quantitative analysis of the structural anomalies, we identified three phonon modes of the monoclinic phase, around 160, 470, and 538 cm^{-1} , which possess an atypical line shape and temperature dependence. We proposed that the distinctive features of all three phonon modes are the result of strong electron-phonon coupling.

Special focus was placed on the electronic contribution to light scattering in magnetite, which also manifests critical characteristics. Indeed, a redistribution of spectral weight takes place in the background intensity around the transition temperature. We proposed that processes from two different types of excitations determine our observations. Namely, Raman scattering from single-particle excitations account for the temperature dependence of the transport properties of magnetite, although here it is not possible to gain any further insight into the conduction mechanism at the origin of our observations. An additional component that prevails in the monoclinic phase was identified with the diffusive dynamics of fluctuation modes.

In INS experiments, critical fluctuations were also observed in the form of diffuse scattering in reciprocal space, associated with central peaks in the inelastic spectra. The $12-26 \text{ cm}^{-1}$ linewidth of the central peak at (0,0,0.75) r.l.u. in the 125-150 K temperature range corresponds to a correlation time on the order of 2.6–5.4 ps, which would further diverge in the absence of the discontinuous transition at T_V . In contrast, in our observations the time scale of the diffusive response around the critical region is on the order of 0.4–0.8 ps. The large ratio between the above time constants suggests different characteristics of the critical fluctuations measured in INS and our experiments. They are supposed to originate, respectively, from excitations with mainly polaronic and electronic character.

Electronic excitations weakly coupled to lattice vibrations are invisible to structure-sensitive probes, such as INS and NRIXS. In contrast, if suitable absorption edges and reflections are chosen, RIXS can serve as a charge-sensitive probe. RIXS experiments are thus needed to provide direct evidence of the electronic excitations discussed earlier, and the wavevector and temperature dependence of possible instabilities should be studied. In particular, based on our observations, they are supposed to give rise to broad central peaks, compared to INS, with ~ 10 meV linewidth around the critical wave vectors.

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APPENDIX

In our theoretical model, we describe the return to equilibrium of a generic ordering field mode upon the perturbation of an external field, in a phenomenological manner, by means of the Landau-Khalatnikov equation of motion,

$$\frac{d\rho_{\boldsymbol{q}}}{dt} = -\gamma \frac{d\mathcal{F}}{d\rho_{-\boldsymbol{q}}} = -(m+\nu|\boldsymbol{q}-\boldsymbol{q}_{c}^{*}|^{2})\rho_{\boldsymbol{q}}(t) - \gamma f_{\boldsymbol{q}}(t),$$
(A1)

with $v = \gamma b$. Here, γ is a phenomenological transport coefficient, which depends on the physics beyond our theoretical model. To extend our treatment to the quantum regime, where the thermal energy is of the same order as the energy scale of the ordering field modes, we turn to the Matsubara

formalism, and we consider the diffusive propagator associated with Eq. (A1) (see Ref. [47] for a similar approach in cuprates),

$$D(\boldsymbol{q}, \omega_m) = \frac{\rho_{\boldsymbol{q}}(\omega_m)}{f_{\boldsymbol{q}}(\omega_m)} = \frac{-\gamma}{|\omega_m| + m + \nu|\boldsymbol{q} - \boldsymbol{q}_c^*|^2}.$$
 (A2)

We compute the dynamical susceptibility, $\chi(\omega_n)$, as the FT of the linear-response function, $R(\tau)$, given by the Kubo formula, again, in a Matsubara representation,

$$\chi(\omega_n) = \int_0^\beta d\tau \ e^{i\omega_n\tau} R(\tau) = \frac{1}{\hbar} \int_0^\beta d\tau \ e^{i\omega_n\tau} \langle T_\tau H_R(\tau) H_R(0) \rangle,$$
(A3)

with $\beta = 1/k_BT$, $\omega_n = 2n\pi/\beta$ the bosonic frequencies, H_R the effective Raman operator, and T_{τ} the time ordering operator. In the Raman processes under consideration, to fulfill wave-vector conservation, mode pairs of opposite wave vectors q and -q are excited together. Therefore, the effective Raman operator is assumed to contain two fluctuation modes,

$$H_R(\tau) = \sum_{q} g_q \, \delta\rho_q(\tau) \delta\rho_{-q}(\tau). \tag{A4}$$

We replace the above expression in Eq. (A3). We develop the correlation factor, taking into account that, to leading order, two fluctuation modes of different wave vectors are independent variables,

$$\chi(\omega_n) = \frac{1}{4\hbar} \sum_{qq'} g_q g_{q'} \int_0^\beta d\tau \ e^{i\omega_n \tau} \ \langle T_\tau \delta \rho_q(\tau) \delta \rho_{-q}(\tau) \delta \rho_{q'}(0) \delta \rho_{-q'}(0) \rangle$$
$$= \frac{1}{2\hbar} \sum_q g_q^2 \int_0^\beta d\tau \ e^{i\omega_n \tau} \ \langle T_\tau \delta \rho_q(\tau) \delta \rho_{-q}(0) \rangle \langle T_\tau \delta \rho_q(\tau) \delta \rho_{-q}(0) \rangle.$$
(A5)

We recognize that the above correlation factors are by definition the diffusive propagator in the time domain, i.e., the inverse FT of Eq. (A2) from Matsubara frequency space to the time domain,

$$D(\boldsymbol{q},\tau) = \frac{1}{\beta} \sum_{n} e^{-i\omega_{n}\tau} D(\boldsymbol{q},\omega_{n}).$$
(A6)

Analytical calculations of the above integral and summation in the complex plane eventually lead to the model function of Eq. (5).

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