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Relevance of thermal disorder in the electronic and spin ultrafast dynamics of iron in low perturbation regime

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Understanding the ultrafast demagnetization of transition metals requires pump-probe experiments sensitive to the time evolution of the electronic, spin and lattice thermodynamic baths. By means of time-resolved photoelectron energy and spin polarization measurements in the low pump fluence regime on iron, we disentangle the different dynamics of hot electrons and demagnetization in the sub-ps and ps time range. We observe a broadening of the Fermi-Dirac distribution, following the excitation of non-thermal electrons at specific region of the iron valence band. The corresponding reduction of the spin polarization is remarkably delayed with respect to the dynamic of electronic temperature. The experimental results are corroborated with a microscopic 3-temperature model highlighting the role of thermal disorder in the quenching of the average spin magnetic moment, indicating Elliot-Yafet type spin-flip scattering as the main mediation mechanism, with a spin-flip probability of 0.1 and a rate of energy exchange between electrons and lattice of 2.5 K fs^{-1} .

INTRODUCTION

Since the first observation of ultrafast demagnetization in a $3d$ ferromagnet following optical excitation [1], a variety of pump-probe techniques [2–9] have addressed this challenging aspect of band structure dynamics in solids. Up to date the observed phenomenology reveals i) a demagnetization within few hundreds of femtoseconds, ii) a partial recovery between approximately 200 fs to 1 ps, and iii) a relaxation to ground state in tens/hundreds of picoseconds. Recently, theoretical and experimental reports made increasingly clear that an explanation in the frame of a Stoner picture is insufficient [10, 11] and that temperature-dependent spin fluctuations play an important role [12, 13]. The statistical disorder in the spin degree of freedom can be included either by using a Weiss-Heisenberg model [14], or an *ad hoc* effective temperature-dependent exchange splitting [15, 16], or by introducing a band-mirroring mechanism [9, 17].

In this context, it is crucial to disentangle the relevance of spin thermal fluctuations from the contribution of electron spin redistribution in occupied and unoccupied bands [3, 9] and from the direct light-spin coupling [18]. An unmediated tool for such investigation is spin-resolved photoemission spectroscopy, only recently emerging in pump-probe experiments thanks to high-repetition rate lasers [8, 9, 19, 20]. In this Letter, we combine two different time-resolved (TR) photoemission techniques to investigate the ultrafast response of Fe(001)-p(1x1)O film, namely i) angular-resolved photoelectron spectroscopy (ARPES) to monitor changes in the electronic energy reservoir across the first Brillouin zone (fBZ) in an energy- and momentum-selective

way [9, 19], and ii) Spin Polarization (SP) analysis of photoelectrons via Mott-scattering experiment to probe the evolution of the magnetic state [21]. We chose the Fe(001)-p(1x1)O surface as it is a well characterized ferromagnetic surfaces and robustness against contamination to ensure reproducible results in long experimental runs [22, 23]. The experiments were performed in the low perturbation regime, to avoid heating the electrons above the Curie temperature and to exclude temporarily collapse of the exchange splitting [24].

We clearly distinguish the thermalized electrons from those directly excited by the pump in a specific band, observing a thermalization time around 300 fs after the pump excitation. The dynamics of the spin polarization turns out to be markedly different with a delayed quenching. We explain the ensemble of the observations following a "microscopic" 3-Temperature Model (m-3TM) [25], which describes the heat transfer between electronic, spin and lattice baths accounting for microscopical scattering parameters, with a Weiss-Heisenberg picture for the spin system. As a result, we identify the ultrafast demagnetization in the low-fluence regime as mainly driven by thermal fluctuations. Fit results yield a spin-flip probability around 0.1 and an electron-lattice energy exchange rate of 2.5 K fs^{-1} .

METHODS

The experiments were performed in the NFFA-Sprint laboratory at IOM-CNR, Trieste [26]. Measurements were conducted in Ultra-High Vacuum (UHV) at a pressure $< 3 \times 10^{-10}$ mbar. A 40 nm thick Fe(001) film was

grown *in situ* in a pressure $p < 2 \times 10^{-9}$ mbar epitaxially on a MgO(001) single crystal. The thickness was estimated by a quartz microbalance. A 30 min annealing at 800 K was followed by a 90 L O₂ exposure ($p = 1 \times 10^{-6}$ mbar at 450 K and a 30 s annealing at 450 K to stabilize the p(1x1)O reconstruction [22]. The O overlayer is needed since it prevents contamination of the Fe surface for weeks in UHV. The sample is homogeneously magnetized along one in-plane easy axis, as proven by measuring vectorial SP across the sample: hereinafter we report only this in-plane direction. The SP values measured in two opposite azimuthal positions of the sample are used to cancel instrumental asymmetries; for time-resolved data, the values at negative delays are employed for such rescaling.

Linearly polarized pump ($h\nu = 1.55$ eV, 50 fs temporal width, s-polarized) and probe ($h\nu = 4.8$ eV, 160 fs, or $h\nu = 21.7$ eV, 110 fs, respectively for TR-SP or TR-ARPES, both s-polarized) pulses were used for time-resolved measurements. Pulsed radiation is generated by non-linear phenomena seeded by a pair of twin Light Conversion PHAROS lasers at 50 kHz, with 1.2 eV photon energy. To measure the SP at phototreshold, the fourth harmonic of one laser, produced by means of BBO crystals ($h\nu = 4.8$ eV, 160 fs temporal width, s-polarized), was used as probe beam. For angle-resolved photoemission (ARPES) spectra we employed a photon energy of 21.7 eV from a High Harmonic Generation (HHG) apparatus [26], pumped by the same laser (110 fs temporal width, s-polarized). The other PHAROS laser feeds an Optical Parametric Amplifier (OPA) delivering an energy-tunable pump beam (in this experiment fixed to 1.55 eV, s-polarized), 50 fs temporal width. The spot diameter, measured exploiting a YAG crystal at sample position, was $100 \times 100 \mu\text{m}$ for the HHG beam, $550 \times 300 \mu\text{m}$ for the 4.8 eV beam and $450 \times 520 \mu\text{m}$ for the pump beam.

The SP of the total photoejected electrons (i.e. integrated in k and energy) was measured with a vectorial Mott polarimeter suitable for multi-hit detection [27]. The sample drain current was simultaneously acquired. TR-ARPES spectra were acquired by a Scienta SES 2002 hemispherical analyser. Additionally, static ARPES measurements were performed at the APE-LE beamline at Elettra synchrotron [23].

ULTRAFAST MAGNETIZATION QUENCHING

In total electron yield (TEY) mode, the contribution of secondary and inelastically scattered electrons can be minimized if photon energy slightly exceeds the sample work function (phototreshold) [28, 29], thus reducing spin-filtering effects [30–32] and preserving the initial-state SP. Threshold photoelectrons are integrated over 10–15 nm of material [33] so that the contribution from

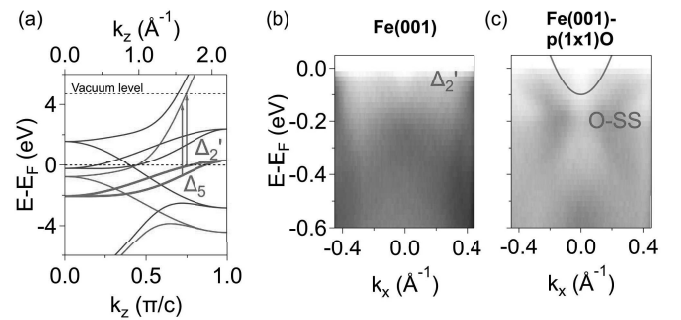


FIG. 1. (a) Density functional theory (DFT) calculations in the LDA approximation for Fe(001), showing the dispersion of the band structure at Γ as a function of k_z along $\Gamma - H$ direction. The available optical transitions to empty states close to the vacuum level for 4.8 eV are highlighted by arrows. (b-c) ARPES spectra along $\bar{\Gamma} - \bar{X}$ direction on clean Fe(001) and Fe(001)-p(1x1)O, measured with 25 eV, p-polarized synchrotron radiation. The parabola encloses the maximum E - k region accessed by 4.8 eV photons according to conservation rules, given a work function of 4.7 eV.

the surface oxygen is negligible. The possible initial states can be identified considering conservation laws in photoemission: with $h\nu = 4.8$ eV the signal arises from the neighborhood of E_F (< 0.1 eV) and from a limited range of k_{\parallel} ($< 0.2 \text{ \AA}^{-1}$). A restriction in k_z is given by the available empty states: according to DFT calculations of bulk Fe bands at Γ_{\parallel} along $\Gamma - H$ direction (Fig. 1a, in agreement with ref. [34]), there are only two possible direct transitions of 4.8 eV towards the vacuum level, with the (majority) $\Delta_{2\uparrow}$ and $\Delta_{5\uparrow}$ bands as initial states. Both transitions lie in the range of k_z expected for photoemission at threshold ($k_{z,PT} \approx 1.4 - 1.7 \text{ \AA}^{-1}$ using inner potential values typically found in literature [34, 35]). The $\Delta_{2\uparrow}$ band can be identified in the small electron-like parabola ($k_F \approx 0.2 \text{ \AA}^{-1}$) observed on clean Fe(001) with $h\nu = 25$ eV (Fig. 1b); at such photon energy, the corresponding k_z verifies the same condition as $k_{z,PT}$ and allows to find $\Delta_{2\uparrow}$ close to E_F at Γ_{\parallel} . Such band is faintly visible also with the p(1x1)O reconstruction (Fig. 1c), although partially covered by the more intense O surface state (O-SS) with $k_F \approx 0.35 \text{ \AA}^{-1}$.

The SP measured with $h\nu = 4.8$ eV is 57(5)%, in excellent agreement with early work on bulk Fe at threshold [36]. A much lower value (20(3)%) is obtained well above threshold ($h\nu = 21.7$ eV), where the contribution of inelastic electrons dominates the TEY and averages over the full band SP. Since in both cases the SP has the same sign, the states probed by 4.8 eV must have majority character, as expected for electrons photoexcited from $\Delta_{2\uparrow}$ and $\Delta_{5\uparrow}$ bands. We can exclude any contribution to the SP from O-SS (of minority character [37]), as it lays outside the parabola in Fig. 1c determined by E - k conservation.

The effect of 1.55 eV pump pulses is presented in Fig.

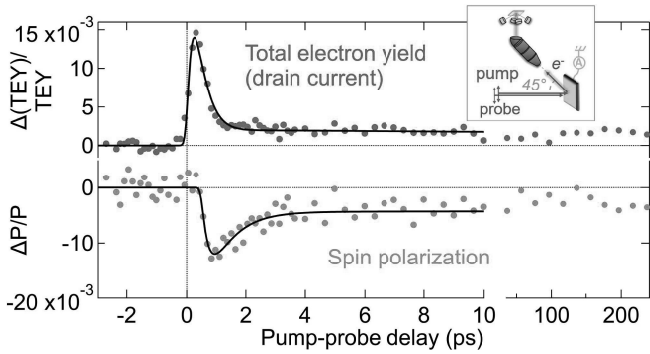


FIG. 2. Time-resolved relative variation of TEY (*top*) and SP (*bottom*) at 1.3 mJ/cm^2 pump fluence, using 4.8 eV probe and 1.55 eV pump. Inset: Experimental geometry.

2: we observe a transient decrease of the SP, partly recovered within few ps, still partially quenched at least up to 200 ps. The quenching depends on the fluence, for values not exceeding 0.3 mJ/cm^2 (Fig. 3). A phenomenological function [7, 8] with the addition of a long-living exponential [5] is used to fit the SP data (as well as the TEY curve in the *top* of Fig. 2):

$$\left\{ \left[Q \left(1 - e^{-\frac{t-t_0}{\tau_Q}} \right) \times \left(e^{-\frac{t-t_0}{\tau_R}} + Q_S e^{-\frac{t-t_0}{\tau_S}} \right) \right] \Theta(t, t_0) \right\} \quad (1)$$

where τ_Q is the quenching time constant and τ_R and τ_S describe respectively the fast and slow recovery (the latter fixed at 200 ps). The function is convoluted with a Gaussian accounting for the temporal resolution (fixed at 160 fs). For the investigated fluences (see Table I), τ_Q and τ_R are in good agreement with ultrafast demagnetization measurements at higher fluences, employing magneto-optical Kerr effect on *3d* transition metals [1, 24, 25, 38], and also specifically on Fe(001) on MgO(001) [5] or W(110) [7]. Our observation of a long-living demagnetized state is in contrast with the results of Tengdin et al. [24], who observe a slow-decaying tail only above the exchange splitting collapse threshold. We argue that the tail is linked to the heat diffusion, which takes hundreds of picoseconds to relax [5, 39].

Given the low photon energy, the peak and the following relaxation trend in the TEY curve in Fig. 2 can be attributed to the broadening of the electron distribution after the pump pulse. However, the TEY increase precedes the SP decrease and the TEY fast relaxation time ($< 300 \text{ fs}$) is significantly smaller than τ_R . Given such

TABLE I. Fit results of the SP dynamics.

Pulse energy (μJ)	Fluence (mJ/cm^2)	Q	τ_Q (fs)	τ_R (fs)
3.4	1.3	2.0%	290 ± 136	772 ± 138
2.3	0.9	1.3%	202 ± 82	436 ± 96

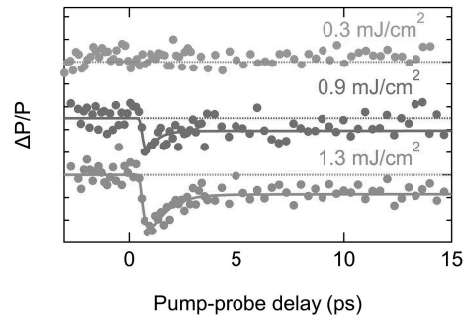


FIG. 3. Time-resolved relative variation of SP as a function of pump fluence.

differences with the electronic distribution evolution simultaneously measured, the observed SP behavior cannot be explained by the redistribution of spin-polarized carriers close to E_F , as proposed in previous experiments on Co [9] and Fe [20]. We also exclude superdiffusive spin currents [9] due to the insulating substrate and the long τ_Q . We thus propose that the observed SP reduction is an effect of the quenching of magnetic moment due to an increase of thermal disorder in the spin degree of freedom after the absorption of optical energy by the electrons. This picture is in agreement with recent theoretical findings on the parameters governing the ultrafast demagnetization [12].

ULTRAFAST DYNAMICS OF ELECTRONS

We now accurately address the induced changes in the electronic distribution over the whole BZ, by means of ARPES with $h\nu = 21.7 \text{ eV}$ as probe (same 1.55 eV pump at 1.3 mJ/cm^2 at normal incidence) imaging the whole BZ by rotating the polar angle, with light polarization parallel to the rotation axis (Fig. 4a). Static ARPES measurements on p(1x1)O-Fe(001) are presented in Fig. 4b. Well-known O-induced states are located in the range from 4 eV to 6 eV binding energy (BE) [40, 41]. Close to E_F , we observe contributions from both bulk Fe and O overlayer (see Supplemental Material, Fig. S5).

TR-ARPES measurements have been carried out in three regions of the BZ (colored rectangles in Fig. 4b), displayed in panels c-e of Fig. 4, corresponding to incidence angles respectively of 15° , 34° and 65° , with effective fluence scaling accordingly. The sharp band in panel f is visible up to 0.4 eV above E_F in the pumped state at t_0 and almost disappearing after 300-500 fs. The integration over the selected k -region (displayed in Fig. 4f) shows that the fastest intensity rise occurs in the range 0.4 - 0.8 eV above E_F (*gold-green curves*), recovering to the equilibrium state within the pump pulse duration. The energy scale and the temporal behavior of such transient state - not observed in the other regions

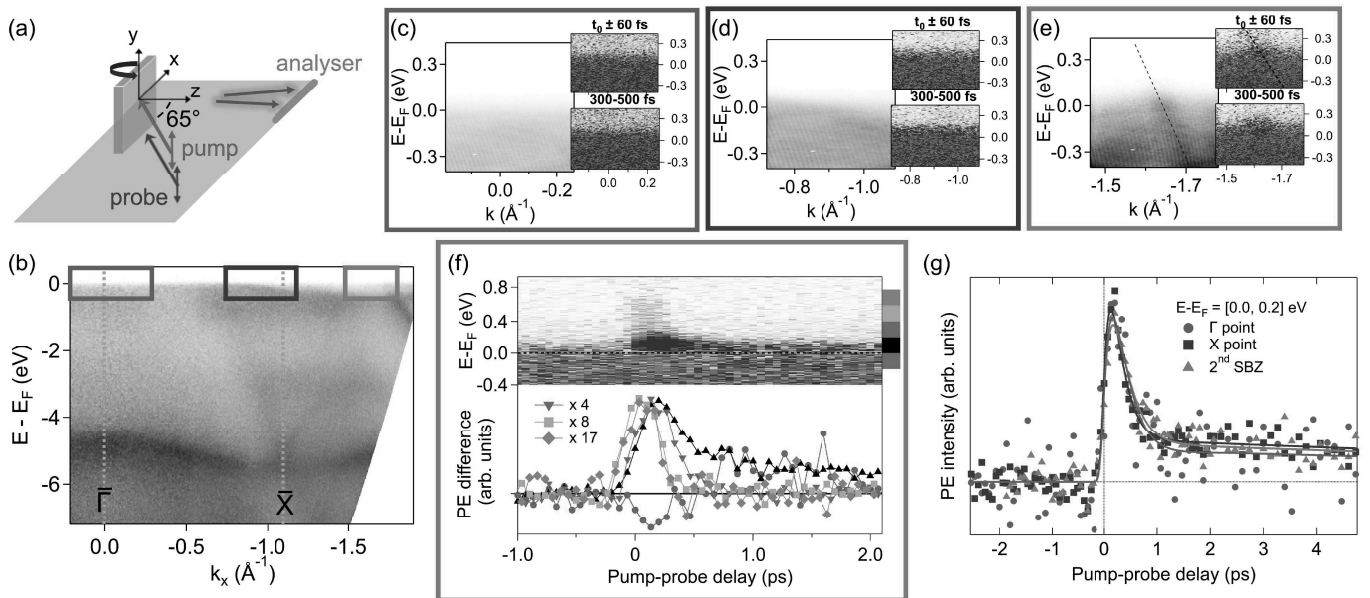


FIG. 4. (a) Cartoon representation of the TR-ARPES experimental geometry. (b) ARPES static measurement at 21.7 eV. (c-e) TR-ARPES with 1.55 eV pump and 21.7 eV probe, measured in the regions of panel (b) highlighted by the colored rectangles. *Main panel*: spectrum averaged over the temporal delays before t_0 . *Insets*: in the *top* (*bottom*) one, difference between the spectrum at $t_0 \pm 60$ fs (300-500 fs) and the average before t_0 (blue positive, red negative). (f) k -integrated spectrum of panel (e) vs delay. *Top*: difference map after subtraction of the average before t_0 (blue positive, red negative). *Bottom*: delay cuts in the energy ranges indicated by the colored rods in the *top* panel, multiplied by arbitrary factors to compare their lineshapes. (g) Comparison of the behavior of thermal electrons in the three momentum regions highlighted in panel (b), with corresponding colors: the intensity difference integrated from 0 eV to 0.2 eV is rescaled to compensate different photoemission intensities due to pump fluence dependence on the incidence angle.

of the BZ - cannot be explained by a broadening of the Fermi-Dirac distribution, hinting at a non-thermal nature [42, 43]. Some tens of femtoseconds later, a peak is reached also at lower energy, within 0.2 eV above E_F (*black curve*), with a concomitant decrease just below E_F (*red curve*), followed by a partial relaxation within 0.5 ps and by a long-living tail (see also Supplemental Material, Fig. S2). This behavior is compatible with a broadening of the Fermi step due to a temperature increase of the electron population, resulting from e-e scattering after the excitation of non-thermal electrons; the fast relaxation is due to thermalization with phonons [44]. The latter kind of trend is mirrored in the other regions of the BZ (Fig. 4g), confirming its thermal nature and the negligible dependence on the specific bands crossing Fermi level, as well as on the fluence (due to different incidence angles) within our low perturbation regime. We stress that such behavior of the electronic distribution around Fermi level is also independent of the coherent size of the p(1x1)O domains (see Supplemental Material, Fig. S6). Exploiting the fitting function in Eq. 1 (temporal width fixed to 110 fs), the thermalization time results 350(50) fs, in agreement with results on Fe/W(110) [19] and Co/Cu(001) [3], and the fast relaxation time 235(25) fs. Consistent results have been obtained with p-polarized probe and different pump energy (see Sup-

plemental Material, respectively Fig. S3 and Fig. S4).

Since non-thermal electrons are observed only at $k_F = 1.65 \text{ \AA}^{-1}$, in the other regions we can describe the electron system using a time-dependent Fermi-Dirac distribution (FDD) at each pump-probe delay. The thermal process can be disentangled from the spectral function by means of the procedure described by Buhlmann et al. [20], which yields a function to be fitted with the FDD $f_{FD}(E; \mu, T_e) = (1 + e^{-(E-\mu)/kT_e})^{-1}$ convoluted with an experimental Gaussian broadening, with chemical potential μ and electronic temperature T_e as free parameters. The former does not change within 1 meV, well below our energy resolution. The extracted T_e is displayed in Fig. 5 as a function of the delay for measurements at \bar{X} (*top*, red dots), increasing up to 360 K (well below the Curie temperature) within few hundreds of fs, and then recovering to a value slightly above equilibrium. The small increase justifies *a posteriori* the assumption of a constant spectral function, *i.e.* no modifications in the band structure and especially in the exchange splitting, as expected for a maximum quenching of 1%.

DISCUSSION

To describe the heat transfer among different degrees of freedom we employ the m-3TM by Koopmans et al. [25], where the microscopic mechanism of phonon-mediated Elliot-Yafet spin-flip scattering is implemented in the temporal evolution of the spin system, treated with a Heisenberg Hamiltonian in the mean-field Weiss approximation. Here we suppose that the measured SP is related to the average magnetic moment m , on the basis of the discussion of Fig. 2. Additionally, following Carpené et al. [42], we add the non-thermal contributions $\partial U_{ee}/\partial t$ and $\partial U_{ep}/\partial t$ to the electronic and lattice differential equations, respectively; such terms describe the energy transfer from non-thermal electrons to thermal electrons and lattice, thus accounting for the slower thermalization compared to the laser pulse shape. This is modeled as a Gaussian profile, with temporal width fixed to 110 fs for T_e and 160 fs for m , and included into $\partial U_{ee}/\partial t$ and $\partial U_{ep}/\partial t$. No additional term is needed in the differential equation for m , since the spin dynamics results unaffected by the presence of non-thermal electrons, within our resolution. The equations read:

$$\gamma_e T_e \frac{dT_e}{dt} = -g_{ep}(T_e - T_p) + \frac{\partial U_{ee}}{\partial t}, \quad (2)$$

$$C_p \frac{dT_p}{dt} = -g_{ep}(T_p - T_e) - k(T_p - T_0) + \frac{\partial U_{ep}}{\partial t}, \quad (3)$$

$$\frac{dm}{dt} = Rm \frac{T_p}{T_C} \left(1 - m \coth \frac{mT_C}{T_e} \right). \quad (4)$$

The lattice specific heat C_p is assumed independent of temperature ($C_p = 3.527 \text{ J/cm}^3\text{K}$) and the electronic specific heat as proportional to T_e through the factor $\gamma_e = 0.7 \text{ mJ/cm}^3\text{K}^2$ [45]. The fit parameters are the electron-phonon coupling g_{ep} and the scaling factor R :

$$R = \frac{8a_{sf}g_{ep}k_B T_C^2 V_{at}}{(\mu_{at}/\mu_B)E_D^2}, \quad (5)$$

The fits of T_e and m curves according to the m-3TM have been performed independently, with consistent results (see Table II) and excellent agreement with data, as displayed in Fig. 5. By averaging the parameters in Table II and solving for a_{sf} in Eq. 5, we find $a_{sf} = 0.104(29)$, in line with values in literature for Ni and Co [25]. The resulting g_{ep} gives a good estimation of the rate for energy exchange between electrons and lattice, $g_{ep}/\gamma_e = 2.5 \text{ K fs}^{-1}$, where the order of magnitude for most metals is around 1 K fs^{-1} [46].

The good agreement with a model in which the magnetic moment variation has intrinsically a thermal and collective origin supports the interpretation of SP at Fermi level in iron as reflecting the behavior of the average magnetic moment. The delayed dynamics of the spin degree of freedom observed here in low perturbation regime is well accounted by this model: the average

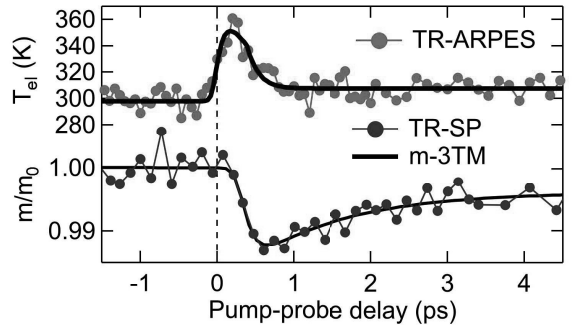


FIG. 5. Electronic temperature (*top*, from the TR-ARPES experiment) and relative magnetic moment (*bottom*, from the TR-SP experiment). Black lines are fits based on the m-3TM model. The temporal alignment has been retrieved using t_0 values obtained by the two independent fit procedures.

magnetic moment starts changing only when the electrons have thermalized. The partial recovery of the magnetic moment within few picoseconds reflects the complete thermalization of the three different baths.

TABLE II. Fit results according to the m-3TM.

Fitted curves	g_{ep} $10^{18} \text{ J}(\text{sm}^3\text{K})^{-1}$	R ps^{-1}
$T_e(t)$, X point	1.5(1)	2.5(5)
$m(t)$, 1.3 mJ/cm ²	1.8(2)	2.5(4)
$m(t)$, 0.9 mJ/cm ²	1.7(3)	2.5(7)

CONCLUSIONS

In conclusion, the electronic temperature and the magnetic moment at E_F after moderate optical excitation behave differently within 2-3 ps: the SP quenches only after the electron gas is fully heated and the thermalization with the lattice is activated, and then recovers with a larger time constant with respect to T_e . On the other hand, the trends of the long-living tail up to hundreds of picoseconds show a clear correspondence, signature of the thermalization of the three reservoirs. Our results demonstrate that in the low-fluence regime the transient spin variation is due to thermal fluctuations, driven by the increase of the electronic temperature upon pump excitation, once non-thermal electrons have transferred their excess energy to the whole electron bath.

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Relevance of thermal disorder in the electronic and spin ultrafast dynamics of iron in low perturbation regime

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Supplemental Material

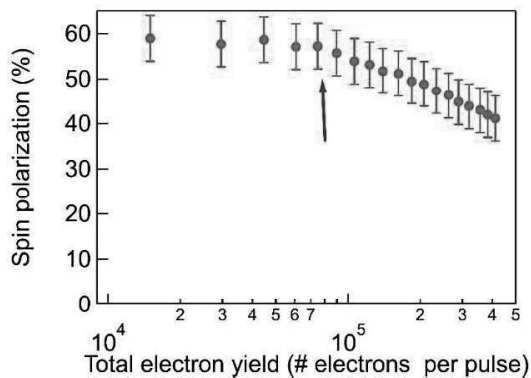


Fig. S1: spin polarization measured with 4.8 eV photons as a function of the photon fluence, expressed as number of electrons per pulse. The blue arrow highlights the highest fluence condition where the measured spin polarization is not affected by two-photon photoemission.

STATIC SPIN POLARIZATION. The spin polarization measurement with laser probe at threshold could be affected by two spurious conditions, space charge (ref. [1]) and two-photon photoemission: the former distorts electron trajectories in a kinetic energy-dependent way, the latter does not fulfil anymore the threshold PES regime condition and thus the signal from secondary electrons becomes dominant. Hence, it is important to find a fluence range where the spin polarization does not change appreciably. Fig. S1 displays a spin polarization fluence scan at $h\nu = 4.8$ eV. The value of spin polarization experiences no change up to a TEY value of $\sim 8 \times 10^5$ electrons per pulse, where a steady decrease kicks off. The arrow highlights the fluence condition where pump-probe measurement at 4.8 eV have been performed. This condition is well into space charge regime, since the corresponding spectra measured with energy analyzer are strongly distorted, but well before two-photon photoemission becomes relevant. We can deduce that the amount of space charge induced by our

laser setup does not influence the spin polarization: as a counterproof, the number of photoemitted electrons per pulse is much lower by orders of magnitude with respect to the case in ref. [1]. Instead, it is likely that the decrease in spin polarization at high fluence is due to two-photon photoemission contributing more and more significantly to the total yield.

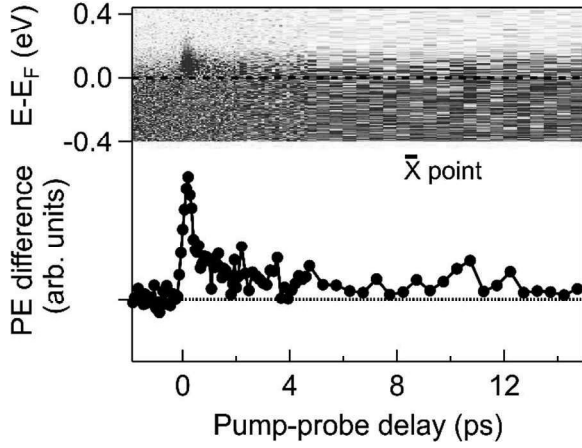


Fig. S2: Time-resolved photoemission with 1.55 eV pump and 21.7 eV probe, integrated in the momentum region highlighted in red in Fig. 2c in main text (close to \bar{X} point), extended to a wider delay region. Top: difference map after subtraction of the average before t_0 (blue positive, red negative). Bottom: delay cuts in the energy range above E_F , highlighted by a black rod in the top panel.

ELECTRON DYNAMICS AT LONG DELAYS. As highlighted in main text, the electronic bath thermalizes within few hundreds fs thanks to e-e scattering, then a fast relaxation occurs due to the thermalization with phonons, but a long-living tail survives, as can be observed in the trends in Fig. 4h in main text. Here we show an extended-delay photoemission measurement up to 15 ps (Fig. S2) to better highlight the long-lasting excited state in the electronic degree of freedom. This trend mirrors the observed behavior for the spin polarization (Fig. 2 in main text).

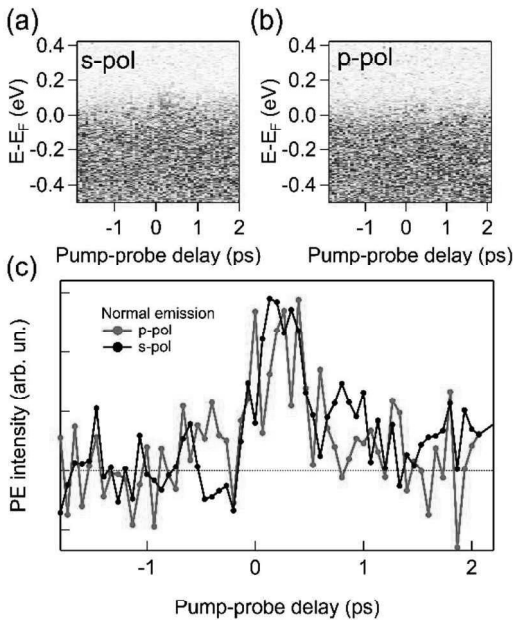


Fig. S3: (a-b) Time-resolved photoemission acquired with s- and p-polarized HHG light as a probe at normal emission. (c) Delay cuts in the energy range within 0.2 eV above Fermi.

PROBE POLARIZATION DEPENDENCE OF ELECTRON DYNAMICS. The combination of the sample mirror planes and the polarization of the probe beam may result in some states at Γ point being hidden by matrix elements in the photoemission process. Hence we repeated the measurement performed with HHG s-polarized probe (displayed in Fig. 4d in the main text, and also shown here in Fig. S3a after angle-integration) with p-polarized probe, resulting in the data shown in Fig. S3b. The comparison of the cuts just above the Fermi level for the two different probe polarizations (Fig. S3c) can be

overlapped with a good degree of confidence, within the experimental sensitivity: we may therefore exclude the presence of any polarization-hidden state in the hot-electron dynamics described in the main text.

PUMP ENERGY DEPENDENCE OF ELECTRON DYNAMICS. The non-thermal electron distribution resulting from a laser pulse in the optical range could vary depending on the allowed or forbidden electronic transitions from the valence band to empty states. In principle, this could also result in different thermalization of the whole electron gas. For this reason, we changed the pump energy from 1.55 to 1.91 eV, and compared in Fig. S4 the respective temporal trend of the electronic distribution measured just above the Fermi level, in the momentum region close to \bar{X} point, with HHG probe (s-polarized). The lineshape of the two delay curves are clearly overlapped, implying that the pump energy has negligible effect on the thermalization time of the electron gas, within our resolution.

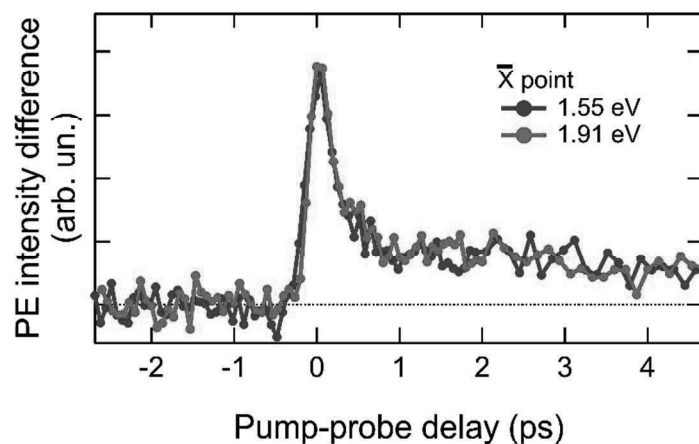


Fig. S4: Delay line cuts integrated within 0.2 eV above Fermi level, for TR-ARPES measurements with pump energy respectively of 1.55 and 1.91 eV and s-polarized HHG light as probe, acquired at normal emission.

ROBUSTNESS OF ELECTRON DYNAMICS AGAINST SURFACE INHOMOGENEITY. The TR-ARPES measurements presented in the main text and in the SI up to this point are performed on a sample ("sample 1") with a slight difference in the oxygen surface reconstruction compared to the sample employed for the TR-SP experiment ("sample 2"). The equilibrium ARPES spectra on these two samples are shown in the left sides of Fig. 5a and 5b, respectively, compared to a synchrotron measurement on a further sample with a well-ordered p(1x1)O reconstruction. In the case of sample 1, the O $2p_y$ bands is less sharp than in sample 2, corresponding to smaller coherent domains of the p(1x1)O reconstruction. In sample 1 there also some additional dispersive bands not visible in the case of sample 2, including the sharp band cutting Fermi level at $k_x = 1.65 \text{ \AA}^{-1}$.

Some of these features could be due to a residual c(2x2)O which we observed on the LEED pattern before any O₂ exposure (not shown). Such oxygen likely intercalates from the substrate during the annealing of the sample after Fe evaporation [2].

Despite such differences in the equilibrium photoemission spectra, the behavior of the Fermi-Dirac upon pumping with 1.55 eV is compatible between the two samples, as shown in the comparison of TR-ARPES measurements on the two samples (Fig. S6). We also stress that such behavior within 0.2 eV from Fermi level is the same, within our temporal resolution, in all the investigated regions of the Brillouin zone, independently of which bands cross the edge (see Fig. 4g in the main text). Such invariance under the degree of order of the surface and under the electron momentum points toward a dominant bulk effect.

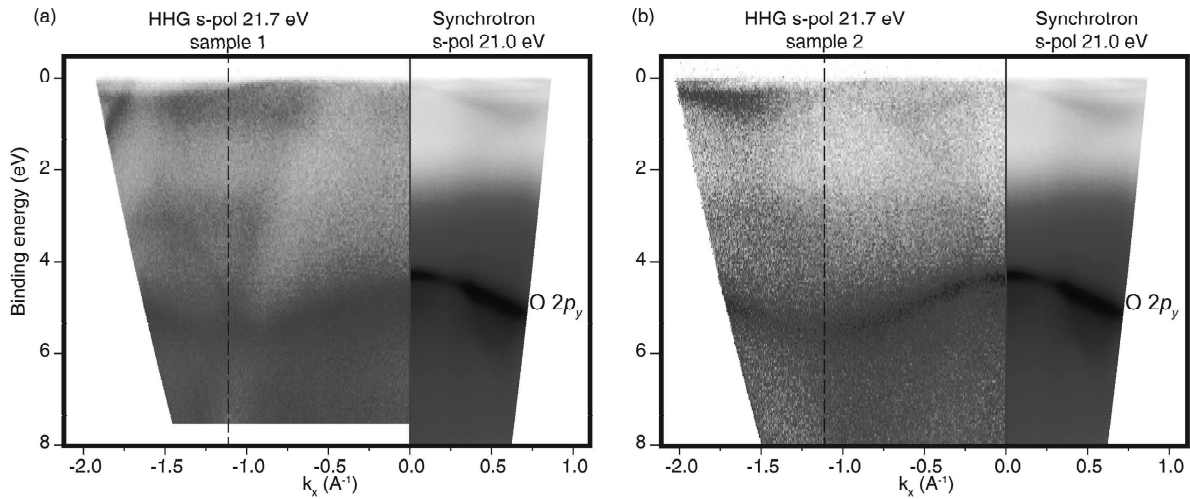


Fig. S5: ARPES measurements with *s*-polarized HHG light (21.7 eV) on two different Fe-*p*(1x1)O surfaces (sample 1 and sample 2). In both pictures, the right side of the image (positive k_x) displays the measurements performed with *s*-polarized synchrotron light at similar photon energy (21.0 eV) on an optimal *p*(1x1)O reconstruction.

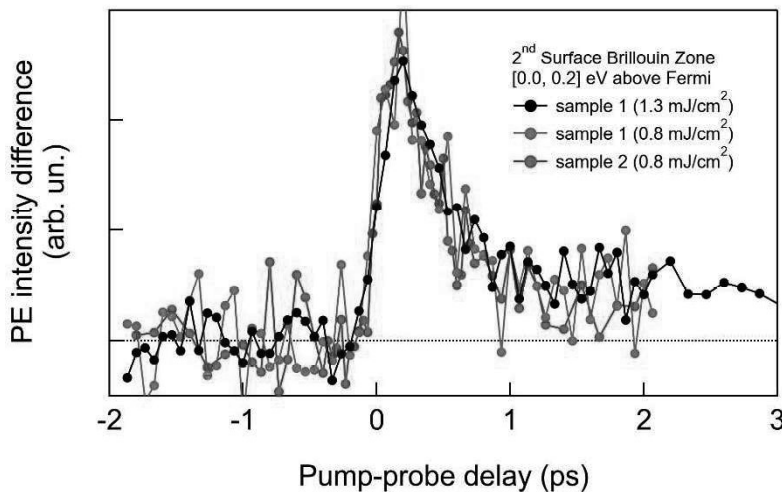


Fig. S6: Delay line cuts integrated within 0.2 eV above Fermi level, for TR-ARPES measurements on sample 1 and sample 2 (pump 1.55 eV), acquired in 2nd Surface Brillouin Zone. The data are normalized to the height of the peak in order to highlight shape differences.

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