Free electron laser-driven ultrafast rearrangement of the electronic structure in Ti

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High-energy density extreme ultraviolet radiation delivered by the FERMI seeded free-electron laser has been used to create an exotic nonequilibrium state of matter in a titanium sample characterized by a highly excited electron subsystem at temperatures in excess of 10 eV and a cold solid-density ion lattice. The obtained transient state has been investigated through ultrafast absorption spectroscopy across the Ti $M_{2,3}$-edge revealing a drastic rearrangement of the sample electronic structure around the Fermi level occurring on a time scale of about 100 fs.
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The study of nonequilibrium condensed matter is a ground-breaking field of research, today only partially explored, essential for the comprehension of elementary processes of paramount importance in physics such as the electron-electron (≈1 fs) and electron-phonon scattering (≈1 ps).[1] Access to nonequilibrium states of matter is possible through ultrafast heating driven by high-energy density femtosecond IR/optical lasers or extreme ultraviolet (EUV)/X-ray free electron lasers (FELs). The latter are particularly appropriate as their short-wavelength radiation can isochorically and uniformly heat up solid samples thus generating in a small volume excited states of matter under controlled conditions.[2] Nonequilibrium conditions originate from the different response of the electron and ion systems to sub-ps light pulses,[3] combined with both the relatively long electron-phonon coupling time and the marked difference between heat capacities of electrons and ions.[4–8] As a consequence, in a few tens of fs, the electron subsystem can reach very high average temperatures ($T_e > 1$ eV), while the ion subsystem remains unaltered ($T_i \simeq 0.025$ eV).[9] Such a unique condition in condensed matter can only persist a few hundreds of fs, and then the thermalization of the electron and ion systems leads to a warm dense matter (WDM) state.[10] Therefore, specific ultrafast methods are demanded to monitor important properties of the exotic state, such as the electronic structure and the electron energy distribution.

Here, we report on an experiment aimed at revealing ultrafast changes in the electron subsystem of a Ti sample driven out of equilibrium ($T_e \gg T_i$) by exposure to intense FEL radiation. The experimental approach consists of high-energy density ultrafast near-edge absorption spectroscopy measurements, carried out across the $M_{2,3}$-edge of Ti ($\varepsilon = 32.6$ eV),

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complemented by reflectivity measurements in the same spectral region. The experiment was carried out at the EIS-TIMEX beamline[11,12] of the FERMI seeded EUV FEL facility.[13,14] Single-pulse FEL irradiation (bandwidth: <100 meV ($\sim$0.3%) FWHM, time duration: $\sim$100 fs, and pulse energy at source: $\sim 100\,\mu$J) was used to generate the desired nonequilibrium transient conditions. The residual transmitted and reflected fractions of the same FEL pulse were measured to characterize the excited sample, as described below.

The experimental setup consisted of a spherical focusing mirror (substrate: Si, coating: 10 nm of Pt, roughness: <0.2 nm RMS, diameter: 30 mm, focal length: 200 mm, and FEL angle of incidence: $\sim 3^\circ$), a 5-axis manipulator equipped with a multi-sample holder, a Si VIS photodiode (UVG20S by Optodiode, sealed in a grounded Al box, coupled with a YAG screen coated with 100 nm of Al on the FEL side) aligned for transmission measurements, a fast EUV Si photodiode (AVG20S by Optodiode, operating with a bias of 150 V) positioned for reflectivity measurements. A Ti self-standing foil (made by Lebow company) of nominal thickness $d = 50$ nm was used for the transmission measurements. Complementary reflectivity measurements were carried out on a Ti deposition (roughness: $\lesssim$1 nm RMS, made by Seso company), consisting of 100 nm of Ti, passivated with 3 nm of TiO_2, on a Si substrate. Homogeneous sample temperature in the sub-ps time scale, essential for ultrafast absorption experiments, was guaranteed by the high critical electron density[2] for radiation at Ti $M_{2,3}$-edge and its attenuation length in Ti comparable to the chosen foil thickness.[15] The reflectivity of the Ti foil at about 30 eV in near-normal incidence is lower than 1%;[15] therefore, the absorption coefficient (μ) has been calculated from transmission measurements by invoking the Lambert-Beer law: $\mu d = \alpha = \ln(I_0/I_1)$, where I_0 and I_1 are the FEL pulse intensities before and after the sample, respectively.

Prior to FEL experiments, EUV absorption spectroscopy measurements at the Ti $M_{2,3}$-edge were performed at the Elettra synchrotron (BEAR beamline[16]) on the same Ti sample to obtain a reference spectrum, shown in Fig. 1. In Fig. 1, one can observe the shape of the rising part of the $M_{2,3}$-edge associated with the atomic transition $[Ar]3d^2 4s^2 \rightarrow [Ar/3\,p\text{-hole}]3d^3 4s^2$. This resonance is known to be affected by autoionization into the previous continuum $[Ar]3d^1 4s^2 \varepsilon f$ leading to a strong Fano lineshape profile.[17]

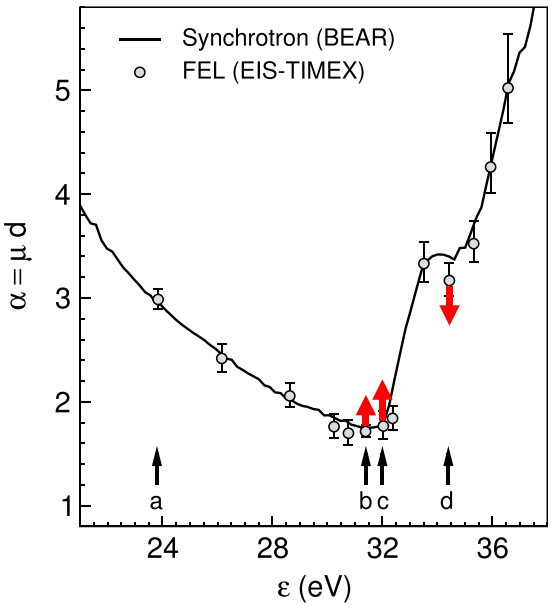

FIG. 1. Absorption spectrum of Ti at ambient conditions in the region of the $M_{2,3}$-edge (32.6 eV). The spectrum has been recorded at the Elettra synchrotron (BEAR beamline) and at the FERMI FEL (EIS-TIMEX beamline). In the latter case, the FEL fluence at the sample was highly attenuated ($F < 1$ mJ cm^{-2}). Vertical black arrows indicate the photon energies (ε) selected for high-fluence absorption and reflectivity measurements (Figs. 2 and 3). Red arrows depict the trend of the ultrafast variation of the absorption coefficient induced by exposure to FEL pulses with fluences in the order of 1 J cm^{-2}. Error bars reflect a 1 - σ confidence interval.

Initially, EUV absorption spectroscopy measurements at EIS-TIMEX have been carried out well below the degradation threshold of the Ti foil (fluence $F \lesssim 1\,\mathrm{mJ\,cm^{-2}}$) in order to record an ultrafast spectrum (open circles in Fig. 1) to be compared with the reference one. This severe level of attenuation has been obtained by increasing the spot size of the FEL up to $120 \times 60\,\mu\mathrm{m}^2$ and by means of a solid state filter (200 nm Al foil, by Luxel company) coupled with a gas attenuator. Reduction of the experimental uncertainty has been achieved acquiring hundreds of measurements on the same sample region for the whole set of selected FEL wavelengths.

With the aim of investigating possible changes in $\alpha(\varepsilon)$ driven by ultrafast heating of the sample, a series of single-shot high-F measurements has been carried out as a function of fluence at the four selected phonon energies indicated by the black vertical arrows in Fig. 1, $\varepsilon = 23.8$, 31.4, 32.0, and 34.4 eV, labeled with letters a, b, c, and d, respectively. The data are presented in Fig. 2. After each single-shot measurement, the sample was moved towards a fresh

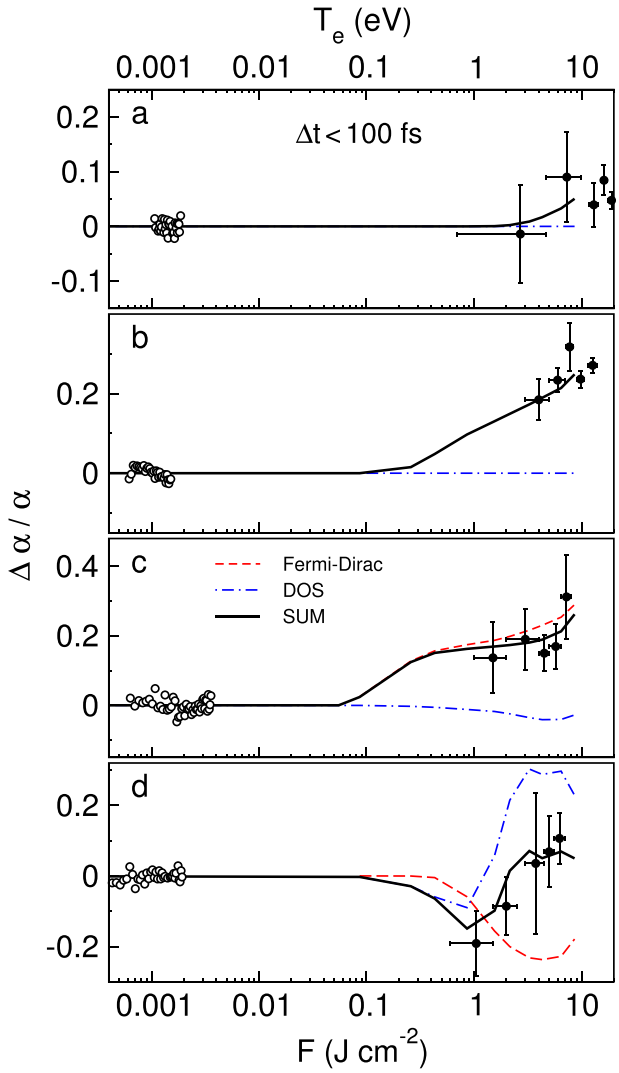

FIG. 2. FEL-driven ultrafast ($\lesssim$100 fs) changes of the absorption coefficient of Ti. The relative absorption variation has been measured as a function of the FEL fluence for four photon energies close to the $M_{2,3}$-edge: (a) 23.8 eV, (b) 31.4 eV, (c) 32.0 eV, and (d) 34.4 eV. Filled circles are obtained by averaging sets of 5–15 single-shot experimental data. The dotted-dashed curves are the relative absorption variation associated with a change in the DOS (Fig. 4, upper panel). The dashed curves represent the relative absorption variation associated with the smearing of the Fermi-Dirac distribution (Fig. 4, bottom panel). The sum of the two effects (Eq. (1)) is drawn as a solid curve. Vertical error bars reflect a 1 - σ confidence interval, horizontal error bars are 2 - σ.

region by a displacement of about 50 μm. The FEL spot at the sample has been decreased down to 100 μm^2 to maximize the F value. An F-range between 1 and 10 J cm^{-2} has been covered using the gas attenuator as a variable intensity filter. In Fig. 2, low-F points (open circles) refer to the measurements carried out below the degradation threshold. Averages of those measurements are represented by the points in Fig. 1. Error bars assigned to high-F data (filled circles) reflect both the inhomogeneity of the Ti foil thickness and the unfavorable signal-to-noise ratio, especially at the most absorbed photon energies. An increase of absorption at high-F values is clearly noticeable, particularly just before the $M_{2,3}$-edge ($\varepsilon = 31.4$ and 32.0 eV, Figs. 2(b) and 2(c)). Experimental data at $\varepsilon = 23.8$ eV (Fig. 2(a)) indicate, within the experimental uncertainty, a similar trend, although the absorption increase appears to be less pronounced. At $\varepsilon = 34.4$ eV (Fig. 2(d)), data are particularly scattered, however one can discern a twofold trend: a tangible attenuation of absorption at intermediate fluences followed by an increase above 1 J cm^{-2}. These findings are in good qualitative agreement with pioneering time resolved x-ray absorption spectroscopy (XAS) measurements carried out on laser-heated metals (Cu L_3-edge,[18] Al K-edge,[19] and Ni L_3-edge[20]). In those experiments, a smearing of the absorption edge was noticed, as indicated by the red arrows in Fig. 1, at least 200 fs after optical laser excitation[20] or after a few ps.[18,19] The current experiment indicates that those changes are already significant in a few tens of fs.

Single-shot reflectivity measurements have been carried out striking the Ti deposition with the FEL beam with an angle of incidence of 6° from the normal at the same photon energies as the absorption data of Fig. 2. The measured experimental signal (ΔR) proportional to the variation of the Ti reflectivity as a function of the fluence is shown in Fig. 3. The maximum fluence

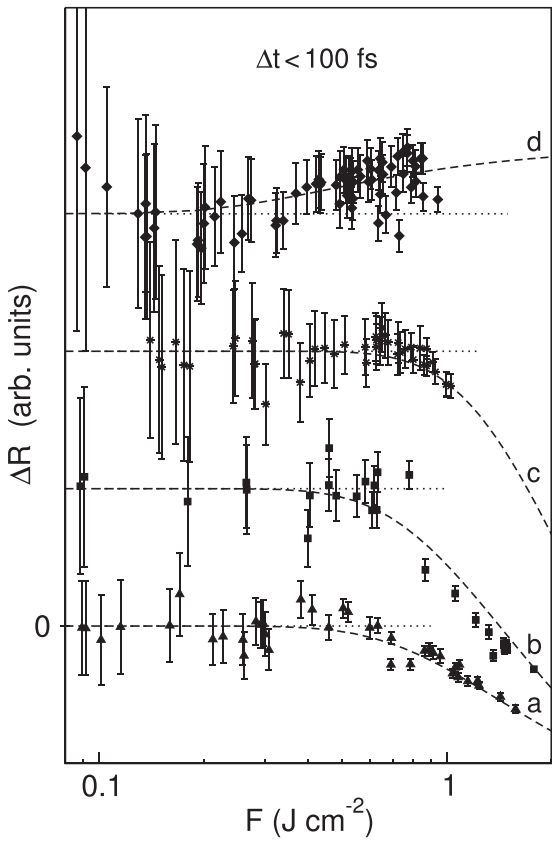

FIG. 3. FEL-driven ultrafast (≲100 fs) changes of the EUV reflectivity of Ti (for the same photon energies of Fig. 2). Data shown in the plot are proportional to the variation of reflectivity and are vertically shifted to facilitate the readability. Dotted horizontal lines indicate the $\Delta R = 0$ level. The dashed curves are guides to the eye. Error bars reflect a 1-σ confidence interval.

at the sample achieved for these measurements is lower than for the absorption measurements as an effect of the Al filter used to block the residual seed laser light, that would have been otherwise detected by the EUV photodiode. A significant drop in reflectivity is noticeable above 0.5 J cm^{-2} at energies below the $M_{2,3}$-edge (dashed curves "a," "b," and "c" in Fig. 3). Contrarily, above the $M_{2,3}$-edge (dashed curve "d" in Fig. 3), the reflectivity exhibits a moderate rise. The same effect has been previously noticed in laser-heated Au at photon energies near the d-s/p interband transition threshold and associated with a rearrangement of the electron population across the Fermi level[5,21] as revealed in Ti by absorption measurement at the $M_{2,3}$-edge.

Absorption measurements appear to be consistent with reflectivity measurements, both confirming the occurrence of ultrafast dramatic changes in the valence electron system of the sample. However, we point out that the experimental data do not allow us to analyze the dynamics of such changes as both absorption and reflectivity measurements reflect a time-averaged behavior of the electron subsystem in the 100 fs time window.

At the relevant photon intensities achieved at the sample in this experiment (≈ 20 J cm^{-2} for $\varepsilon = 23.8$ eV), the ponderomotive potential locally exerted by the FEL pulse on the Ti electrons is still negligible;[22] therefore, we operate in a weak radiation field regime where time-dependent perturbation theory can be applied.[23] In our case, a single FEL pulse delivers a maximum of 10^{12} photons at the Ti sample that corresponds to an average of about 10 photons per Ti atom distributed in a temporal window of about 100 fs. For the 3p electrons of Ti, the recombination process, dominated by a super Coster-Kronig transition, is expected to be particularly fast ($\tau \leq 1$ fs).[24] Therefore, despite the relatively high photon density, alterations of the absorption coefficient triggered by absorption saturation of the $M_{2,3}$ core level are negligible. Finally, the absorption coefficient is expected to be very sensitive the *d*-projected density of states (*d*-DOS) that is calculated to be the 90% of the total DOS across the Fermi level in Ti.[25]

In light of these considerations, the changes shown in Figs. 2 and 3 can be principally ascribed to temperature-driven dynamics of the valence electrons in Ti that involve a marked rearrangement of electron population across the Fermi level and—possibly—an alteration of the DOS. As the absorption coefficient is proportional to the product of the empty states distribution and the DOS, we focus our attention on the absorption data. Assuming that the dipole matrix element is invariant upon the interaction between the FEL pulse and the sample, the relative variation of absorption in first approximation can be expressed in terms of two functions of the photon energy (ε) and electron temperature (T_e),

$$\frac{\Delta\alpha}{\alpha}(\varepsilon, T_e) = c_g(\varepsilon)\, g(\varepsilon, T_e) + c_\phi(\varepsilon)\, \phi(\varepsilon, T_e), \tag{1}$$

where $g(\varepsilon, T_e)$ provides the variation of the DOS in Ti, $\phi(\varepsilon, T_e)$ is the variation of the empty electronic states probability distribution. Variations are intended between a final high temperature state and the initial room temperature (*RT*) condition. Parameters $c_\phi(\varepsilon)$ and $c_g(\varepsilon)$ are used as scaling factors to obtain the agreement between the theoretical curves and the experimental data.

Functions $g(\varepsilon, T_e)$ are derived from recent density functional theory DOS calculations carried out for Ti under nonequilibrium conditions (hot electrons and cold ion lattice).[25] In Fig. 4 (top panel), the Ti DOS used in this work is reported for three different electron temperatures. The DOS curves are obtained by a convolution procedure between the calculated DOS[25] and a Lorentzian function with width $\gamma = 0.05$ eV accounting for the spectral broadening associated with the short lifetime of the 3*p* core hole in Ti. The vertical black arrows in Fig. 4 refer to the electron energies sampled in our experiment (see also arrows in Fig. 1 and related panels in Fig. 2). Functions $\phi(\varepsilon, T_e)$ are obtained using the Fermi-Dirac distribution f ($\phi(\varepsilon, T_e) = f(\varepsilon, T_e^{RT}) - f(\varepsilon, T_e)$) assuming that the valence electrons are thermalized upon interaction with the FEL pulse.[25]

Functions $g(\varepsilon, T_e)$ and $\phi(\varepsilon, T_e)$, weighted by $c_g(\varepsilon)$ and $c_\phi(\varepsilon)$ parameters, are represented in Fig. 2 as a function of the fluence by dotted-dashed and dashed curves, respectively. The Fermi

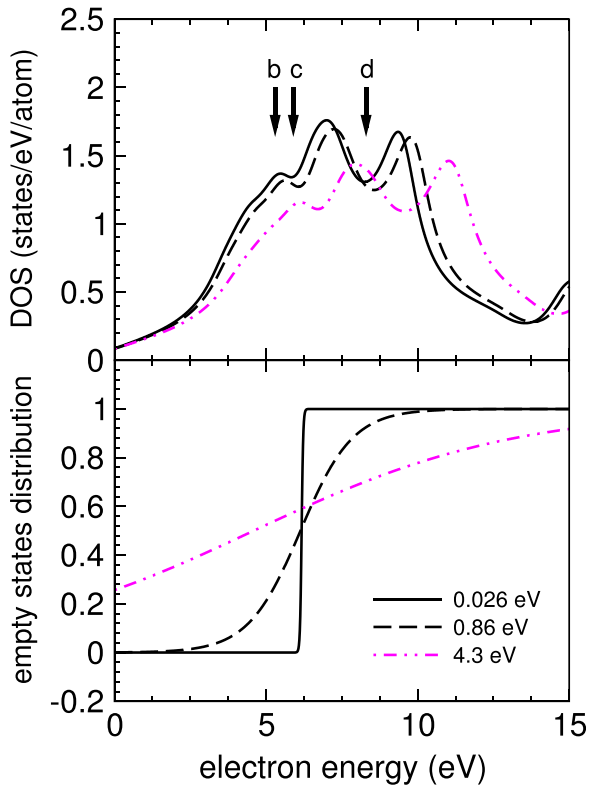

FIG. 4. DOS (here convoluted with a Lorentzian of width $\gamma = 0.05$ eV) and distribution of empty electronic states calculated in Ref. 25 for nonequilibrium Ti at three different electron temperatures (0.026 eV, 0.86 eV, and 4.3 eV).

level has been located at $\varepsilon = 32.3$ eV. Moreover, the empirical relation F (J cm^{-2}) $= T_e$ (eV) has been utilized in good agreement with both previous self-reflectivity experiments on Ti[26] and two-temperature model (TTM) calculations showing that, for fluences under consideration here, T_e in excess of 1 eV can be reached during the pulse FEL absorption.[18,21] Clearly, the estimated electron temperatures represent a time-average on the 100 fs time window. The employed weight factors values are $c_g(\varepsilon) = 0.0$, 0.0, 0.2, and 3.0 and $c_\phi(\varepsilon) = 0.1$, 0.35, 0.4, and 0.8 for the photon energies labeled *a*, *b*, *c*, and *d*, respectively. The pronounced energy dependence of the weight factors is ascribed to the used DOS and electron distribution functions.

The resulting relative absorption variations are given by the solid curves in Fig. 2. The overall accord between theoretical curves and experimental data is good and appears to validate the approach of Eq. (1). Below the Fermi level, changes due to DOS variation are negligible (Figs. 2(a) and 2(b)), and the rise in absorption mainly reflects the Fermi-Dirac smearing at high temperatures. Across the Fermi level, changes in the DOS begin to affect the absorption coefficient (Fig. 2(c)). Above the Fermi level (Fig. 2(d)), both the DOS and electron distribution changes alter the absorption. The experimental data trend reflects both the absorption gain given by the marked DOS increase at high T_e (predicted in Ref. 25) and the absorption decrease related to the presence of hot electrons in conduction band.

In conclusion, we have shown that within an exceedingly short time window comparable to that of the FEL pulse ($\lesssim$100 fs), the valence electron system in Ti exhibits drastic ultrafast dynamics, activated by fs-heating, that alter both the opacity and reflectivity of the sample. We have modeled the relative variation of absorption as the sum of two theoretical curves describing, respectively, the variation of the DOS and the variation of the empty electronic states fraction across the Fermi level. This approach seems to validate recent calculations[25] that predict a radical rearrangement of the electron distribution and a shift towards higher energies of the DOS in laser-heated Ti. Further investigations are demanded to clarify if the Fermi-Dirac

function can be used to model the electron distribution upon exposure to an intense FEL pulse ($t \lesssim 100$ fs). Future improvements of the experimental method promise to use FEL-based ultrafast near-edge XAS as a possible alternative to other techniques[10,20,27,28] for DOS evaluation in metals under nonequilibrium conditions as well as to gain access to sub-100 fs electronic dynamics in excited condensed matter with the opportunity of studying unexplored laser-driven hidden phases of the electronic structure.

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