Nonlinear absorption of an X-ray pulse during the formation of warm dense matter

A bright, ultrashort X-ray pulse is used to transiently create and characterize warm dense copper. As the pulse intensity is increased, the opacity of copper is strongly altered. The recorded X-ray absorption spectra, substantiated by a theoretical electronic structure model, provide insight into the non-equilibrium electron dynamics during the formation of warm dense matter.

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The question

X-ray free-electron lasers (XFELs) open the door to nonlinear X-ray science and probes of dynamical processes with femtosecond resolution. During an intense X-ray pulse, an atom is likely to absorb more than one photon[1]. At achievable XFEL intensities of 10^{15}–10^{18} W cm^{-2}, a solid material becomes heavily ionized, creating hot electrons, with ionic cores initially at their equilibrium positions. This massive ionization provides a controlled pathway to systematically create a state in between solid and plasma[2,3], termed warm dense matter (WDM). WDM is also transiently created in inertial confinement fusion and is ubiquitous in the inner cores of giant planets. Nevertheless, much remains unknown about WDM. For example, there are questions relating to the electron temperatures that can be achieved and the time it takes to equilibrate temperatures between the electrons and ionic cores to create WDM at equilibrium. We addressed these questions using X-ray absorption near-edge structure (XANES) spectroscopy to investigate the behaviour of both free and bound electrons during the formation of WDM.

The observation

Femtosecond XANES is a powerful technique to study the dynamics of the electronic and structural properties of matter. Hitherto, it has been applied to investigate optically excited WDM[4]. Here, we focused a bright, ultrafast X-ray pulse with a photon energy centred at the copper L edge on a thin copper foil and measured its transmitted spectrum at different applied intensities. Ionization of the 2*p* inner atomic shell and secondary processes, such as Auger–Meitner decay and electron impact ionization, give rise to a hot, non-equilibrium distribution of electrons with vacancies in the 3*d* band. This state opens new excitation pathways and drastically alters the X-ray absorption spectrum (Fig. 1a). With an increase in intensity, the copper foil initially absorbs more X-ray radiation, that is, exhibits a nonlinear effect called reverse saturable absorption. However, further increasing the intensity reverts the trend and results in a decrease in absorption, that is, the foil demonstrates another nonlinear effect called saturable absorption (Fig.1b).

The WDM state that is created is challenging to describe theoretically. Modelling of WDM typically involves a plasma description to account for ionization and electron dynamics. Conversely, correlation effects, electronic bonds and hybridization, which cannot be neglected at the density of solids, require a solid-state physics treatment. The transient, non-equilibrium character of this WDM state further complicates the task. Our solution required a new model that combines plasma and solid-state approaches. In particular, our calculations of the transient absorption spectra show that the transition from reverse saturable absorption to saturable absorption is due to increased ionization of the 3*d* band, which leads to reduced electron screening of the nuclear charge, and hence to a shift of the absorption spectrum to higher energies, out of the spectral window of the applied XFEL.

Future directions

Although our theoretical model yields qualitative agreement with the observations, further developments are required to realize a self-consistent electronic-structure theory and spectral response functions to quantitatively capture X-ray absorption spectra for out-of-equilibrium WDM. These models could, in turn, be benchmarked by future refined measurements. In addition, understanding material opacity under these extreme conditions is crucial for inertial confinement fusion[5], to ensure that the energy used for compression of the imploding capsule does not escape, enabling efficient fusion reactions.

The drastic changes in the electronic structure of solid copper occur within the 15-fs duration of the XFEL pulse. Although movement of atomic nuclei during such a short timescale is negligible, our calculations show that this duration is comparable to the equilibration time of the electrons. This result suggests that our time-integrated XANES spectra might contain notable contributions from the non-equilibrium evolution stages.

It would therefore be particularly interesting to investigate the formation of the WDM state observed in this work with higher temporal resolution, in a pump–probe manner. This approach would provide access to experimental measurements of ionization dynamics and enable even more accurate tests of non-equilibrium electronic structure models. Such experiments are within reach: the prospect of attosecond XFEL pulses and attosecond transient absorption spectroscopy capabilities will further widen the applicability of the presented approach in the study of matter under extreme conditions.

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EXPERT OPINION

"Previous work on this topic reported either reverse saturable absorption (RSA) or saturable absorption (SA); this paper reports the observation of the RSA–SA transition, through measurements over a wide XFEL intensity range. The use of X-ray absorption near edge structure (XANES) spectroscopy measurements, together with the well-established electron kinetic Boltzmann and FEFF simulations for XANES, is very innovative and enables tracking of the ultrafast electronic behaviour under intense X-ray irradiation. This is an important advance for the community." **Marion Harmand, CNRS-PIMM, Paris, France.**

FIGURE

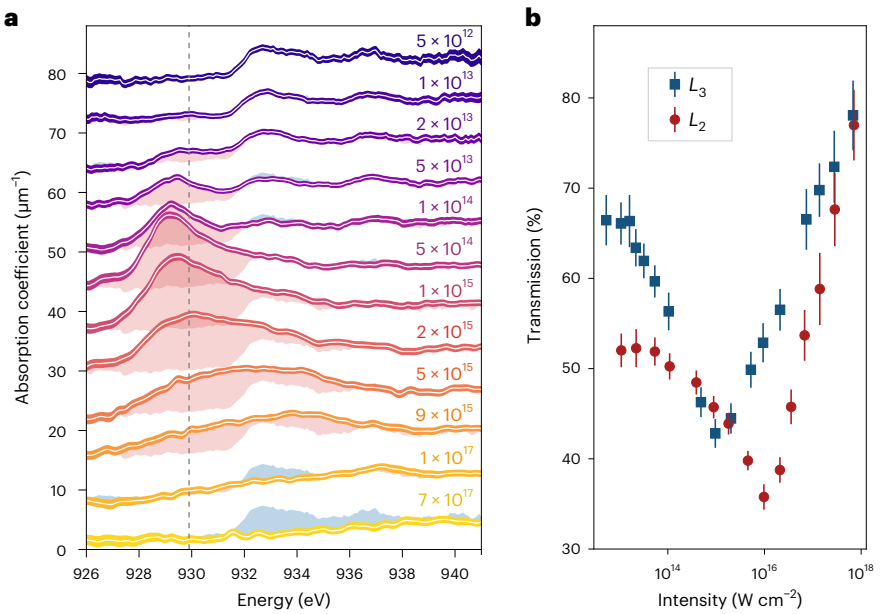

Fig. 1 | Transient absorption and transmission of an intense XFEL pulse through a 100-nm-thick copper foil. a, Absorption spectra at the copper L_3 edge at various XFEL intensities (in W cm^{-2}). The coloured areas around each spectrum indicate the 95% confidence interval. The red areas show the reverse saturable absorption regions, where the spectrum exhibits increased absorption with respect to that of the low-intensity spectrum at 5×10^{12} W cm^{-2}. Conversely, the blue areas show the saturable absorption regions of the spectra, with decreased absorption compared with that of the low-intensity spectrum. **b**, Transmission of the XFEL pulse as a function of its intensity at the copper L_2 and L_3 edges, showing the transition from reverse saturable absorption to saturable absorption. The error bars indicate the 95% confidence interval.

BEHIND THE PAPER

Previously, WDM has been created in the laboratory by heating with optical laser pulses, and theoretical descriptions of this regime have focused on thermodynamic equilibrium. The description of the quasi-instantaneous creation of WDM with XFEL pulses is a more delicate task because the initial energy deposition is distinct from the optical case. We initially used a pure plasma-based model to gain understanding and interpret the observed spectra. Upon request of the referees to predict the X-ray absorption spectrum for this WDM state, we were inspired to develop a theoretical model that merges the perspectives of a pure plasma description with self-consistent electronic structure theory. We owe this new theory to a fruitful collaboration with Joshua J. Kas and John J. Rehr. This work has motivated us to further develop the theoretical framework of WDM and to benchmark our models by attosecond transient X-ray absorption experiments. **N.R. & L.M.**

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FROM THE EDITOR

"There are several elements of this work that stand out: the spectrally resolved measurements, the observation of a transition from reverse saturable absorption to saturable absorption and the state-of-the-art theoretical calculations. The results will be useful for benchmarking non-equilibrium models of electronic structure in warm dense matter." **Editorial Team, *Nature Physics*.**