Supplementary Materials for

Probing electron and hole colocalization by resonant four-wave mixing spectroscopy in the extreme ultraviolet

Horst Rottke*, Robin Y. Engel, Daniel Schick, Jan O. Schunck, Piter S. Miedema, Martin C. Borchert, Marion Kuhlmann, Nagitha Ekanayake, Siarhei Dziarzhytski, Günter Brenner, Ulrich Eichmann, Clemens von Korff Schmising, Martin Beye, Stefan Eisebitt*

*Corresponding author. Email: rottke@mbi-berlin.de (H.R.); eisebitt@mbi-berlin.de (S.E.)

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**Frequency conversion: monochromatic plane wave limit** Throughout the following derivation we will employ the cgs system of units. The corresponding geometry is sketched in Fig. S1. The Maxwell equations in the frequency domain used to determine the propagation of the non-linearly generated electromagnetic waves in the LiF crystal while applying intense driving radiation fields are:

\[
\nabla \times E_\omega(x) = \frac{i \omega}{c} B_\omega(x) \quad \nabla B_\omega(x) = 0 \quad (S1)
\]

\[
\nabla \times B_\omega(x) = -\frac{i \omega}{c} D_\omega(x) \quad \nabla D_\omega(x) = 0. \quad (S2)
\]

\(\omega\) represents the frequency of the generated electromagnetic wave, \(E_\omega(x)\) its electric field, \(B_\omega(x)\) the corresponding magnetic induction, \(D_\omega(x)\) the dielectric displacement, and \(c\) is the speed of light. The equations above assume the magnetic permeability of the nonlinear medium to be equal to 1. The dielectric displacement is linked to the electric field strength via:

\[
D_\omega(x) = \epsilon(\omega) E_\omega(x) + 4\pi P_\omega(x) \quad (S3)
\]

with \(\epsilon(\omega)\) the linear dielectric constant of the medium at the frequency \(\omega\) of the generated electromagnetic wave and \(P_\omega(x)\) the nonlinear contribution to the polarization of the medium at that frequency. The polaritation wave, in our case, is driven by the propagation of the FEL and NIR laser fields in the LiF crystal. We assume \(\epsilon(\omega)\) to be a scalar quantity since the LiF crystal is of cubic symmetry. Absorption of LiF at the frequency of the generated wave renders \(\epsilon(\omega)\) a complex quantity with its imaginary part being positive. On the vacuum side from where the FEL and NIR laser beams enter the crystal the same Maxwell equations above apply with \(\epsilon(\omega) = 1\) and \(P_\omega(x) = 0\).

The Maxwell equations together with relation (S3) for the dielectric displacement can be combined into an inhomogeneous wave equation for the electric field \(E_\omega(x)\):

\[
\Delta E_\omega + \epsilon(\omega) \left(\frac{\omega}{c}\right)^2 E_\omega = -4\pi \left[\left(\frac{\omega}{c}\right)^2 P - \frac{1}{\epsilon(\omega)} k P\right] \exp(i k x), \quad (S4)
\]
Figure S1: **The geometry used to measure the FWM signal in reflection off a polished (100)-cut LiF interface to vacuum.** The blue arrows represent the FEL (X), the red the NIR (I) laser beam, and the purple ones the generated sum-/difference-frequency beams (FWM). They propagated in a common plane of incidence which we choose to be the $x$-$z$-plane of a suitably chosen Cartesian coordinate system with the $z$-axis normal to the LiF surface and parallel to one of the LiF cubic crystal axes. The $x$-$y$-axes of this coordinate system in the LiF surface plane were rotated by $22.5 \pm 2.5^\circ$ with respect to the two in plane crystal axes of the LiF crystal used as shown in the inset.
with solutions subject to the additional restriction:

\[ \nabla E_\omega = -\frac{4\pi i}{\varepsilon(\omega)} k P \exp(ikx). \]  

(S5)

Relations (S4) and (S5) assume \( P_\omega(x) \) to be a plane wave \( P_\omega(x) = P \exp(ikx) \), implying the driving FEL and NIR laser fields are plane waves. The wave vector \( k \) of the polarization wave is fixed by the specific nonlinear conversion process and by the wave vectors of the driving laser fields in the medium. We further assume the polarization wave to propagate in the \((x, z)\)-plane of a suitably chosen coordinate system with \( k = (k_x, 0, k_z) \) determined by the common plane of incidence of the FEL and NIR radiation on the LiF crystal. \( P \) represents the constant amplitude of the polarization wave. We do not account for any potential nonlinear polarization of the medium bound to the vacuum-material interface.

The Maxwell equations (S1) and (S2) imply specific boundary conditions at the vacuum-medium interface (the \( x, y \)-plane). Namely, the magnetic induction has to be continuous across the boundary. Also the \( x \)- and \( y \)-components of the electric field (i.e. the components parallel to the interface) and the \( z \)-component of the dielectric displacement (i.e. the component perpendicular to the interface) have to be continuous across the interface. In the medium the generated electromagnetic wave propagates with the polarization wave \( P_\omega(x) \) into the medium, i.e. towards \( z = -\infty \). The generated wave on the vacuum side propagates towards \( z = +\infty \). There is no wave on the vacuum side propagating towards the interface at \( z = 0 \) at the frequency \( \omega \). Since the wave vector of the polarization wave \( k = (k_x, 0, k_z) \) has zero \( y \)-component so the wave vectors of the generated waves in vacuum and in the medium have a zero \( y \)-component. The electric field of the generated wave on the vacuum side can thus be represented by \( E_r(x) = A_r \exp(ik_r x) \) with \( k_r = (k_{rx}, 0, k_{rz}) \), transverse electric field amplitude \( A_r(k_r, A_r = 0) \) and \( k_{rz} > 0 \). The dispersion relation \( k_r^2 = (\omega/c)^2 \) ties the \( x \)- and \( z \)-components of the wave vector together.
The inhomogeneous wave equation (S4) in the medium for this geometry is solved with the Ansatz
\[ \mathbf{E}_M(\mathbf{x}) = \tilde{\mathbf{E}}(z) \exp(i\tilde{k}_x x). \] (S6)

It results in an inhomogeneous ordinary second order differential equation for the amplitude \( \tilde{\mathbf{E}}(z) \)
\[ \frac{d^2 \tilde{\mathbf{E}}(z)}{dz^2} + \tilde{k}_z^2 \tilde{\mathbf{E}}(z) = \frac{4\pi}{\epsilon(\omega)} \left[ k(kP) - \epsilon(\omega) \left( \frac{\omega}{c} \right)^2 P \right] \exp(ik_z z). \] (S7)

\( \tilde{k}_z \) used in Eq. (S7) is set via the dispersion relation \( \tilde{k}_z^2 = \epsilon(\omega) (\omega/c)^2 - \tilde{k}_x^2 \) with the real and imaginary parts of \( \tilde{k}_z \) chosen to be negative in order to make sure the generated electric field in the nonlinear medium propagates with the polarization wave towards \( z = -\infty \) and force absorption in the medium. With these restrictions the general solution of Eq. (S7) reads
\[ \tilde{\mathbf{E}}(z) = \tilde{\mathbf{A}} \exp(i\tilde{k}_z z) + \frac{H}{\tilde{k}_z^2 - k_z^2} \exp(ik_z z), \] (S8)

with
\[ H = \frac{4\pi}{\epsilon(\omega)} \left[ k(kP) - \epsilon(\omega) \left( \frac{\omega}{c} \right)^2 P \right]. \] (S9)

The amplitude vectors \( \mathbf{A}_r \) of the electric field on the vacuum side [Eq. (1) of the main text] and \( \tilde{\mathbf{A}} \) are still free constants. They are fixed by the boundary conditions at the vacuum-medium interface, by Eq. (S5) in the medium, and by the fundamental condition that the electric field vector on the vacuum side must be transverse to the propagation direction of the wave. The boundary conditions can only be satisfied provided the still free wave vector components \( \tilde{k}_x \) and \( k_{rx} \) satisfy the condition \( \tilde{k}_x = k_{rx} = k_x \), i.e. they have to be equal to the \( x \)-component of the wave vector of the nonlinear polarization wave. Via the dispersion relations on the vacuum side and in the medium then also the \( z \)-components \( \tilde{k}_z \) and \( k_{rz} \) are fixed subject to the constraints \( k_{rz} > 0 \) and the real and imaginary parts of \( \tilde{k}_z \) have to be negative.

Involving these constraints results in the explicit form for the electric field amplitude \( \mathbf{A}_r \) on
the vacuum side given in Eq. (2) of the main text and in

\[ \tilde{A} = \frac{4\pi}{\epsilon(\omega) [k_z - \epsilon(\omega) k_{rz}]} \left\{ P_x + (k_z - \epsilon(\omega) k_{rz}) \left[ k \times P \right]_y \frac{k_z}{k_z^2 - k_{rz}^2} \right\} \begin{bmatrix} \tilde{k}_z \\ 0 \\ -k_{ry} \end{bmatrix} + 4\pi \left( \frac{\omega}{c} \right)^2 \frac{k_z - k_{rz}}{k_z - k_{rz}} \frac{P_y}{k_z^2 - k_{rz}^2} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \]  

(S10)

The result Eq. (S8) for the dependence of the electric field in the medium on the \( z \)-coordinate may be rewritten in the form

\[ \tilde{E}(z) = \left[ \tilde{A} + \frac{H}{k_z^2 - k_{rz}^2} + H \exp[i(k_z - \tilde{k}_z)z] - 1 \right] \exp(i\tilde{k}_z z) \]  

(S11)

to emphasize the role of phase matching in the nonlinear process provided the wave vectors \( k \) of the nonlinear polarization wave in the medium and \( \tilde{k} \) of the generated wave become equal [meaning \( \tilde{k}_z = k_z \) in Eq. (S11)]. In the limit of phase matching the \( z \) independent term in square brackets in Eq. (S11), namely \( \tilde{A} + H/(k_z^2 - k_{rz}^2) \), does not become singular. This can be seen when explicitly evaluating it using the expressions for \( H \) and \( \tilde{A} \) given above. Phase matching means the \( z \) dependent term in square brackets in Eq. (S11), i.e. the amplitude of the electric field of the generated wave in the medium grows in proportion to the propagation length \( z \) in the medium. However, one has to keep in mind that absorption in the medium will counteract the buildup of the electric field. Absorption enters via the imaginary part of \( \tilde{k}_z \) in \( \exp(i\tilde{k}_z z) \) in the expression for the electric field in Eq. (S11). After a certain propagation length absorption will always win over the linear buildup in \( z \) of the wave’s amplitude.

**The directions of emission of the sum- and difference-frequency beams on the vacuum side** In the plane wave approximation used here the wave vector components of the XUV and NIR beams impinging on the LiF crystal in the surface plane of the crystal determine the corresponding component of the wave vector of the polarization wave in the crystal. We represent
these wave vectors by \( \mathbf{k}^{\text{vX}} = (k_x^{\text{vX}}, 0, k_z^{\text{vX}}) \) and \( \mathbf{k}^{\text{vI}} = (k_x^{\text{vI}}, 0, k_z^{\text{vI}}) \) for the XUV and NIR beams, respectively, using the coordinate system defined in Fig. S1. Boundary conditions for the electromagnetic fields imply that the \( x \)-components of the wave vectors of the XUV and NIR beams (in plane components), which drive the nonlinear processes, do not change when passing into the LiF crystal. Then the \( x \)-components of the wave vectors of the polarization waves in the medium are \( k_x = k_x^{\text{vX}} ± 2k_x^{\text{vI}} \), respectively. According to the previous section \( k_x \), in turn, equals the \( x \)-component of the wave vectors of the generated electromagnetic fields on the vacuum side \( (k_{rx} = k_x) \). Based on the dispersion relation for the sum- and difference-frequency fields on the vacuum side they thus propagate along the wave vector \( \mathbf{k}_r = \left( k_x, 0, \sqrt{(\omega/c)^2 - k_x^2} \right) \).

Nonlinear reflection thus occurs at an angle \( \theta = \arcsin(c k_x/\omega) \) relative to the LiF surface normal.

**The nonlinear polarization amplitude \( \mathbf{P} \)** For the particular nonlinear processes of four-wave mixing relevant to our experiment, namely sum- and difference-frequency mixing, the amplitude \( \mathbf{P} \) of the nonlinear polarization of the medium is linked to the specific third order nonlinear susceptibility tensors \( \chi^{(3)}(-\omega_X - 2\omega_I; \omega_X, \omega_I, \omega_I) \) and \( \chi^{(3)}(-\omega_X + 2\omega_I; \omega_X, -\omega_I, -\omega_I) \), respectively. Based on the cubic symmetry of the LiF crystal (space group \( m\overline{3}m \)) these tensors have 27 elements which are different from zero with only four of them being independent (36). Skipping the dependence on the frequencies for convenience, one complete set of independent, non-zero elements is \( \chi^{(3)}_{x,x,x,x}, \chi^{(3)}_{x,x,y,y}, \chi^{(3)}_{x,y,x,y} \) and \( \chi^{(3)}_{x,y,y,x} \) in a Cartesian frame of reference with axes coinciding with the crystal axes (36).

According to the experimental situation, the LiF crystal’s \( z \)-axis is chosen to coincide with the \( z \)-axis of the plane of incidence of the FEL and NIR laser beams, whereas the crystal’s \( x \)-axis enclosed an angle \( \varphi \) with the \( x \)-axis of the plane of incidence (see Fig. 2 of the main text and Fig. S1). The components of the electric field amplitudes of the FEL and NIR plane waves
in the nonlinear medium may be written \( E_X = (E_{X,x}, 0, E_{X,z}) \) and \( E_I = (E_{I,x}, 0, E_{I,z}) \). This representation uses as the frame of reference the \( x- \) and \( z- \) axes of the plane of incidence together with the corresponding orthogonal \( y- \) axis (see Fig. S1). The \( y- \) components of the amplitudes are both set to zero, assuming the waves are polarized in the plane of incidence, just as in the setting in the experiment. With these assumptions the components of the induced nonlinear polarization \((P_x, P_y, P_z)\) in the same reference frame can be written as

\[
P_x = \chi^{(3)}_{x,x,x,x} E_{X,x} E_{I,x}^2 \left( \sin^4 \varphi + \cos^4 \varphi \right) + \chi^{(3)}_{x,x,y,y} E_{X,x} E_{I,x}^2 + \left( \chi^{(3)}_{x,y,x,x} + \chi^{(3)}_{x,y,y,x} \right) E_{X,z} E_{I,x} E_{I,z} + \frac{1}{2} \left( \chi^{(3)}_{x,x,y,y} + \chi^{(3)}_{x,y,x,x} + \chi^{(3)}_{x,y,y,x} \right) E_{X,x} E_{I,x} \sin^2 2\varphi
\]

\[
P_y = \frac{1}{4} \left( \chi^{(3)}_{x,x,y,y} + \chi^{(3)}_{x,y,x,y} + \chi^{(3)}_{x,y,y,x} - \chi^{(3)}_{x,x,x,x} \right) E_{X,x} E_{I,x} \sin 4\varphi
\]

\[
P_z = \chi^{(3)}_{x,x,x,x} E_{X,z} E_{I,z}^2 + \chi^{(3)}_{x,x,y,y} E_{X,z} E_{I,x}^2 + \left( \chi^{(3)}_{x,y,x,y} + \chi^{(3)}_{x,y,y,x} \right) E_{X,x} E_{I,x} E_{I,z}
\]

This relation supposes the nonlinear process of sum-frequency mixing. For difference-frequency mixing one has to use the complex conjugate NIR electric field strength components in the equations for the amplitude components of the nonlinear polarization above.

In our model for \( \chi^{(3)} (-\omega_X - 2\omega_I; \omega_X, \omega_I, \omega_I) \) and \( \chi^{(3)} (-\omega_X + 2\omega_I; \omega_X, -\omega_I, -\omega_I) \) we simplify the LiF crystal symmetry by assuming the medium to be invariant under the full rotation group. This introduces an additional constraint for the independent elements of the nonlinear susceptibility tensor above. Only three of the four elements remain independent (36)

\[
\chi^{(3)}_{x,x,y,y} + \chi^{(3)}_{x,y,x,y} + \chi^{(3)}_{x,y,y,x} - \chi^{(3)}_{x,x,x,x} = 0
\]

As one may already expect, this relation eliminates any dependence of the induced nonlinear polarization \( P \) above on the angle \( \varphi \).

**The model for the linear and 3rd order susceptibilities** Computing the amplitude of the electric field [Eq. (2), main text] of the reflected sum- and difference-frequency waves requires
the knowledge of the linear dielectric constant $\epsilon(\omega)$ of LiF in the relevant photon energy range. We constructed $\epsilon(\omega)$ using the measured linear reflection off LiF in Fig. 1(B). As a model a set of seven discrete, homogeneously broadened resonances was chosen to simulate the structures found in the reflection curve by suitably choosing their positions, widths and oscillator strengths. Since the measurement did not determine the reflection coefficient but only represents the intensity of the reflected light the absolute scale for the dielectric constant had to be set using a reported LiF absorption coefficient at a certain photon energy. We utilized the measured absorption coefficient at 70 eV photon energy reported in (37).

The relation
\[
\alpha(\omega) = \sum_j \frac{f_j}{\omega_j^2 - \omega^2 - i\gamma_j\omega}
\] (S16)
for the microscopic reaction of LiF to an applied electric field in the frequency range of interest is employed to determine the dielectric constant. It is based on molecular polarizability (see (38)). The adjustable parameters $\omega_j$, $\gamma_j$ and $f_j > 0$ are chosen so as to simulate the measured LiF reflection in Fig. 1B. The Clausius-Massotti equation
\[
\alpha(\omega) = 3\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2}
\] (S17)
links the microscopic reaction to the dielectric constant $\epsilon$ (38). The parameters $\omega_j$, $\gamma_j$ and $f_j > 0$ which result in a reasonable fit of the experimental linear reflection off LiF (see Fig. 1(B), the blue line) are gathered in Table S1. The real and imaginary parts of the dielectric constant $\epsilon$ corresponding to this choice of parameters are shown in Fig. S2. The main, $p$-type LiF core exciton resonance is responsible for the maximum of the imaginary part of $\epsilon(\omega)$ at 62 eV while its low energy shoulder represents the suspected $s$-type core exciton.

The calculation of the third order nonlinear susceptibility tensor is based on the expression for its components given in reference (36) (page 93). Since in the experiment a detectable, resonance like enhancement of sum- and difference-frequency mixing was observed when the
Table S1: The parameters entering Eq. (S16) for the linear microscopic reaction of LiF to an applied electromagnetic wave in the photon energy range between \( \approx 58 \) eV and \( \approx 72 \) eV which is relevant to the experiment. The dielectric constant based on this choice of the parameters allows to reasonably reproduce the experimental LiF reflectivity as shown in Fig. 1(B) of the main text.

| \( j \) | 1 (1s)(2s) | 2 (1s)(2p) | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| \( \omega_j / \text{eV} \) | 49.82 | 60.97 | 62.07 | 63.12 | 65.0 | 67.55 | 69.92 |
| \( \gamma_j / \text{eV} \) | 50.0 | 1.1 | 0.79 | 1.3 | 2.4 | 4.3 | 1.45 |
| \( f_j / \text{eV}^2 \) | 42.0 | 0.59 | 1.54 | 0.17 | 0.92 | 2.77 | 0.75 |

Figure S2: The calculated linear dielectric constant \( \epsilon(\omega) \) in the photon energy range between 58 eV and 72 eV. The blue line shows the real and the orange one the imaginary part of \( \epsilon \).
LiF p-type exciton was involved, we only take this resonance into account together with the suspected s-type excitonic resonance in determining the dependence of $\chi^{(3)}$ on the driving FEL photon energy. In the expression for $\chi^{(3)}$ we therefore only employ the resonance positions $\omega_j$ and widths $\gamma_j$ in Table S1 with $j = 2, 3$ which correspond to these resonances. For the nonlinear susceptibility we neglect a dipole coupling of the s-type exciton to the ground electronic state. However, we take into account a potential, dipole allowed coupling of this s- to the p-type main exciton. We use this simplification since we think the main influence on sum- and difference-frequency generation by the suspected s-type exciton is through its coupling to the p-type exciton which is driven by the applied NIR laser field. The NIR photon energy of 1.55 eV does not much exceed the separation in energy of these two excitons ($\omega_3 - \omega_2 = 1.1$ eV according to Table S1).

With this simplification, only two dipole matrix elements are relevant in the expression for $\chi^{(3)}$: one for the dipole coupling of the p-type exciton to the ground state and one for the coupling of the s- and p-type excitons. For lack of information on the details of the electronic states involved we use one-electron atomic dipole matrix elements and assume the ground state is represented by a state with angular momentum $l = 0$ (s-state) and the excited states involved by $l = 0$ and $l = 1$ with magnetic quantum numbers $m_l = 0, \pm 1$. This approach reduces the number of free parameters in the expression for $\chi^{(3)}$ to two radial dipole matrix elements and modifies the symmetry of the LiF crystal from cubic to full rotational symmetry. Based on this simplified model we calculate the independent components of $\chi^{(3)}$ which in turn provide the amplitude of the third order nonlinear polarization amplitude $P$ needed for the determination of the sum- and difference-frequency yields for comparison with the experimental result.

**Calibration of the MUSIX spectrometer** Incidence angles on the sample surface were determined in situ with a photodiode on the diffractometer. The sample’s crystal axes were deter-
mined *ex situ* through Laue diffraction and the sample orientation was transferred by mounting
the sample on a holder with an azimuthal Vernier scale.

For every setting of the spectrometer grating, a calibration measurement was performed
by varying the undulator gap of the FEL. This generated a discrete series of different FEL
photon energies reflected off the LiF sample via the grating onto the CCD camera, bypassing the
installed beam-block. To prevent saturation of the CCD, two 295 nm thick zirconium attenuator
foils were placed in the FEL beam path. This allowed calibrating the MUSIX spectrometer
against the wavelength measurement implemented in the beamline (39). In addition, the overall
consistency of the various estimated parameters used in the MUSIX spectrometer transmission
calculations described below was verified by asserting an agreement between the number of
photons measured by an x-ray gas-monitor-detector (XGMD) (34) in the FEL beamline and by
the MUSIX spectrometer’s CCD at different wavelengths. As no linear reflectivity spectrum of
the sample was acquired with the MUSIX spectrometer, a flat sample reflectivity of 0.05 % was
used in this consistency check.

**Estimation of the total number of photons generated in the FWM processes** The read out
CCD camera counts were converted to an estimated number of incident photons assuming 50 %
of these photons (a conservative estimate of the CCD’s quantum efficiency) were converted into
electron-hole-pairs in the silicon chip with a bandgap of 3.1 eV. Each electron created one digital
count in the analog-to-digital converter of the CCD, according to the manufacturer information
for the readout frequency employed in the experimental runs. On the way from the LiF sample
to the CCD the photons have been reflected off the MUSIX spectrometer gating and passed an
aluminum filter foil. For the grating a 15 % diffraction efficiency in first order is assumed. The
aluminum filter transmission (thickness 200 nm) is retrieved from tabulated data (40, 41). We
also accounted for an estimated 12.5 nm aluminum-oxide layer on each side of the filter.
In a similar way, the total number of FEL photons impinging on the LiF sample per pulse was derived from pulse energy measurements using an XGMD upstream (34). Following the XGMD the FEL beam passed a silicon filter, three beamline mirrors, beam width limiting apertures and the incoupling mirror for the NIR laser beam which all reduced the FEL pulse energy before reaching the sample. The number of photons per pulse was determined from the total pulse energy measured by the XGMD, assuming 7% of the measured pulse energy was due to FEL harmonics that were absorbed by the downstream 411 nm thick silicon filter. Its transmission for the fundamental FEL beam was calculated from tabulated transmission data assuming a 12.5 nm thick silicon oxide layer on each side (40, 41). Likewise, based on tabulated data (40, 41), the reflectivities of the three beamline mirrors (2° grazing angle of incidence and coated with nickel, gold and platinum, respectively) were taken into account. Wavefront-sensor measurements during beamline-alignment further suggested 25% transmission through the beamline apertures and the incoupling mirror for the IR laser beam due to clipping.

Comparing the photon flux on the CCD to that measured by the XGMD in the calibration measurements described above lends some credence to the transmission estimates made here. However, a significant uncertainty of the scaling factors involved remains. Therefore, we refer to the total number of FEL photons arriving on the LiF sample and photons generated in the FWM processes, which we show in Figs. 3 and 4 of the main text, as estimates only.

**The experimental dependence of the frequency conversion on the NIR laser pulse energy**

To further support the nature of the observed nonlinear processes we determined the dependence of the frequency conversion yield on the pulse energy of the NIR laser pulses. In the regime of low conversion, as was the case in the experiment, the dependence is expected to be quadratic. This is just what the experiment indicates as Fig. S3 shows. The measurement was done with the FEL photon energy set to 59.25 eV. The nonlinear process involved was sum-frequency mixing.
Figure S3: **Dependence of the number of sum-frequency photons generated on the NIR laser pulse energy arriving on the LiF crystal.** The FEL laser photon energy was set to 59.25 eV, i.e. 3-photon resonant with the LiF exciton resonance ($\omega_{\text{exc}} = \omega_X + 2\omega_I$). The blue line represents a fit to the data points using a quadratic polynomial in the NIR pulse energy.

three-photon resonant with the LiF exciton resonance ($\omega_{\text{exc}} = \omega_X + 2\omega_I$). The data points allow fitting a quadratic dependence of the sum-frequency photon yield on the NIR laser pulse energy (blue line in Fig. S3).
REFERENCES AND NOTES

1. H. Danino, I. Freund, Parametric down conversion of x rays into the extreme ultraviolet. *Phys. Rev. Lett.* **46**, 1127–1130 (1981).

2. K. Tamasaku, K. Sawada, E. Nishibori, T. Ishikawa, Visualizing the local optical response to extreme-ultraviolet radiation with a resolution of $\lambda/380$. *Nat. Phys.* **7**, 705–708 (2011).

3. A. Schori, C. Bömer, D. Borodin, S. P. Collins, B. Detlefs, M. Moretti Sala, S. Yudovich, S. Shwartz, Parametric down-conversion of x rays into the optical regime. *Phys. Rev. Lett.* **119**, 253902 (2017).

4. T. E. Glover, D. M. Fritz, M. Cammarata, T. K. Allison, S. Coh, J. M. Feldkamp, H. Lemke, D. Zhu, Y. Feng, R. N. Coffee, M. Fuchs, S. Ghimire, J. Chen, S. Shwartz, D. A. Reis, S. E. Harris, J. B. Hastings, X-ray and optical wave mixing. *Nature* **488**, 603–608 (2012).

5. S. Shwartz, M. Fuchs, J. B. Hastings, Y. Inubushi, T. Ishikawa, T. Katayama, D. A. Reis, T. Sato, K. Tono, M. Yabashi, S. Yudovich, S. E. Harris, X-ray second harmonic generation. *Phys. Rev. Lett.* **112**, 163901 (2014).

6. R. K. Lam, S. L. Raj, T. A. Pascal, C. D. Pemmaraju, L. Foglia, A. Simoncig, N. Fabris, P. Miotti, C. J. Hull, A. M. Rizzuto, J. W. Smith, R. Mincigrucci, C. Masciovecchio, A. Gessini, E. Allaria, G. De Ninno, B. Diviacco, E. Roussel, S. Spampinati, G. Penco, S. Di Mitri, M. Trovò, M. Danailov, S. T. Christensen, D. Sokaras, T.-C. Weng, M. Coreno, L. Poletto, W. S. Drisdell, D. Prendergast, L. Giannessi, E. Principi, D. Nordlund, R. J. Saykally, C. P. Schwartz, Soft x-ray second harmonic generation as an interfacial probe. *Phys. Rev. Lett.* **120**, 023901 (2018).

7. F. Bencivenga, R. Cucini, F. Capotondi, A. Battistoni, R. Mincigrucci, E. Giangrisostomi, A. Gessini, M. Manfredda, I. P. Nikolov, E. Pedersoli, E. Principi, C. Svetina, P. Parisse, F. Casolari, M. B. Danailov, M. Kiskinova, C. Masciovecchio, Four-wave mixing experiments with extreme ultraviolet transient gratings. *Nature* **520**, 205–208 (2015).
8. L. Foglia, F. Capotondi, R. Mincigrucci, D. Naumenko, E. Pedersoli, A. Simoncig, G. Kurdi, A. Calvi, M. Manfreda, L. Raimondi, N. Mahne, M. Zangrando, C. Masciovecchio, F. Bencivenga, First evidence of purely extreme-ultraviolet four-wave mixing. Phys. Rev. Lett. 120, 263901 (2018).

9. F. Bencivenga, R. Mincigrucci, F. Capotondi, L. Foglia, D. Naumenko, A. A. Maznev, E. Pedersoli, A. Simoncig, F. Caporaletti, V. Chiloyan, R. Cucini, F. Dallari, R. A. Duncan, T. D. Frazer, G. Gaio, A. Gessini, L. Giannessi, S. Huberman, H. Kapteyn, J. Knobloch, G. Kurdi, N. Mahne, M. Manfreda, A. Martinelli, M. Murnane, E. Principi, L. Raimondi, S. Spampinati, C. Spezzani, M. Trovò, M. Zangrando, G. Chen, G. Monaco, K. A. Nelson, C. Masciovecchio, Nanoscale transient gratings excited and probed by extreme ultraviolet femtosecond pulses. Sci. Adv. 5, eaaw5805 (2019).

10. E. Shwartz, S. Shwartz, Difference-frequency generation of optical radiation from two-color x-ray pulses. Opt. Express 23, 7471–7480 (2015).

11. C. P. Schwartz, S. L. Raj, S. Jammuch, C. J. Hull, P. Miotti, R. K. Lam, D. Nordlund, C. B. Uzundal, C. Das Pemmaraju, R. Mincigrucci, L. Foglia, A. Simoncig, M. Coreno, C. Masciovecchio, L. Giannessi, L. Poletto, E. Principi, M. Zuerch, T. A. Pascal, W. S. Drisdell, R. J. Saykally, Angstrom-resolved interfacial structure in buried organic-inorganic junctions. Phys. Rev. Lett. 127, 096801 (2021).

12. J. R. Rouxel, D. Fainozzi, R. Mankowsky, B. Rösner, G. Seniutinas, R. Mincigrucci, S. Catalini, L. Foglia, R. Cucini, F. Döring, A. Kubec, F. Koch, F. Bencivenga, A. A. Haddad, A. Gessini, A. A. Maznev, C. Cirelli, S. Gerber, B. Pedrini, G. F. Mancini, E. Razzoli, M. Burian, H. Ueda, G. Pamfilidis, E. Ferrari, Y. Deng, A. Mozzanica, P. J. M. Johnson, D. Ozerov, M. G. Izzo, C. Bottari, C. Arrell, E. J. Divall, S. Zerzane, M. Sander, G. Knopp, P. Beaud, H. T. Lemke, C. J. Milne, C. David, R. Torre, M. Chergui, K. A. Nelson, C. Masciovecchio, U. Staub, L. Patthey, C. Svetina, Hard x-ray transient grating spectroscopy on bismuth germanate. Nat. Photonics 15, 499–503 (2021).
13. J. D. Gaynor, A. P. Fidler, Y.-C. Lin, H.-T. Chang, M. Zuerch, D. M. Neumark, S. R. Leone, Solid state core-exciton dynamics in NaCl observed by tabletop attosecond four-wave mixing spectroscopy. *Phys. Rev. B* **103**, 245140 (2021).

14. R. Haensel, C. Kunz, B. Sonntag, Measurement of photoabsorption of the lithium halides near the lithium $K$ edge. *Phys. Rev. Lett.* **20**, 262–264 (1968).

15. W. Olovsson, I. Tanaka, P. Puschnig, C. Ambrosch-Draxl, Near-edge structures from first principles all-electron Bethe-Salpeter equation calculations. *J. Phys. Condens. Matter* **21**, 104205 (2009).

16. S. T. Pantelides, Electronic excitation energies and the soft-x-ray absorption spectra of alkali halides. *Phys. Rev. B* **11**, 2391–2411 (1975).

17. J. R. Fields, P. C. Gibbons, S. E. Schnatterly, Electronic excitations in LiF: 10-70 eV. *Phys. Rev. Lett.* **38**, 430–434 (1977).

18. E. L. Shirley, Li 1s near-edge spectra in six lithium halides. *J. Electron Spectros. Relat. Phenomena* **137-140**, 579–584 (2004).

19. W. Olovsson, I. Tanaka, T. Mizoguchi, P. Puschnig, C. Ambrosch-Draxl, All-electron Bethe-Salpeter calculations for shallow-core x-ray absorption near-edge structures. *Phys. Rev. B* **79**, 041102 (2009).

20. A. B. Kunz, J. C. Boisvert, T. O. Woodruff, Li $K$-edge soft-x-ray absorption in LiF. *Phys. Rev. B* **30**, 2158–2162 (1984).

21. A. B. Kunz, J. T. Devreese, T. Collins, The role of the electronic polaron in the soft X-ray absorption of the lithium halides. *J. Phys. C Solid State Phys.* **5**, 3259–3263 (1972).

22. B. F. Sonntag, Observations of “forbidden” soft-x-ray transitions: Li $K$ absorption in LiF. *Phys. Rev. B* **9**, 3601–3602 (1974).
23. W. Gudat, C. Kunz, H. Petersen, Core exciton and band structure in LiF. *Phys. Rev. Lett.* **32**, 1370–1373 (1974).

24. T. Sato, R. Letrun, H. J. Kirkwood, J. Liu, P. Vagović, G. Mills, Y. Kim, C. M. S. Takem, M. Planas, M. Emons, T. Jezynski, G. Palmer, M. Lederer, S. Schulz, J. Mueller, H. Schlarb, A. Silenzi, G. Giovanetti, A. Parenti, M. Bergemann, T. Michelat, J. Szuba, J. Grünert, H. N. Chapman, A. P. Mancuso, Femtosecond timing synchronization at megahertz repetition rates for an X-ray free-electron laser. *Optica* **7**, 716 (2020).

25. S. Schulz, I. Grguraš, C. Behrens, H. Bromberger, J. T. Costello, M. K. Czwalinna, M. Felber, M. C. Hoffmann, M. Ilchen, H. Y. Liu, T. Mazza, M. Meyer, S. Pfeiffer, P. Prędki, S. Schefer, C. Schmidt, U. Wegner, H. Schlarb, A. L. Cavalieri, Femtosecond all-optical synchronization of an X-ray free-electron laser. *Nat. Commun.* **6**, 5938 (2015).

26. J. Duris, S. Li, T. Driver, E. G. Champenois, J. P. MacArthur, A. A. Lutman, Z. Zhang, P. Rosenberger, J. W. Aldrich, R. Coffee, G. Coslovich, F.-J. Decker, J. M. Glownia, G. Hartmann, W. Helml, A. Kamalov, J. Knurr, J. Krzywinski, M.-F. Lin, J. P. Marangos, M. Nantel, A. Natan, J. T. O’Neal, N. Shivaram, P. Walter, A. L. Wang, J. J. Welch, T. J. A. Wolf, J. Z. Xu, M. F. Kling, P. H. Bucksbaum, A. Zholents, Z. Huang, J. P. Cryan, A. Marinelli, Tunable isolated attosecond X-ray pulses with gigawatt peak power from a free-electron laser. *Nat. Photonics* **14**, 30–36 (2020).

27. A. A. Maznev, R. Mincigrucci, F. Bencivenga, V. Unikandanunni, F. Capotondi, G. Chen, Z. Ding, R. A. Duncan, L. Foglia, M. G. Izzo, C. Masciovecchio, A. Martinelli, G. Monaco, E. Pedersoli, S. Bonetti, K. A. Nelson, Generation and detection of 50 GHz surface acoustic waves by extreme ultraviolet pulses. *Appl. Phys. Lett.* **119**, 044102 (2021).

28. E. Berger, S. Jammuch, C. B. Uzundal, C. Woodahl, H. Padmanabhan, A. Amado, P. Manset, Y. Hirata, Y. Kubota, S. Owada, K. Tono, M. Yabashi, C. Wang, Y. Shi, V. Gopalan, C. P. Schwartz, W. S. Drisdell, I. Matsuda, J. W. Freeland, T. A. Pascal, M. Zuerch, Extreme ultraviolet second harmonic generation spectroscopy in a polar metal. *Nano Lett.* **21**, 6095–6101 (2021).
29. D. Popova-Gorelova, D. A. Reis, R. Santra, Theory of X-ray scattering from laser-driven electronic systems. *Phys. Rev. B* **98**, 224302 (2018).

30. R. Cohen, S. Shwartz, Theory of nonlinear interactions between x rays and optical radiation in crystals. *Phys. Rev. Res.* **1**, 033133 (2019).

31. J. R. Rouxel, M. Kowalewski, K. Bennett, S. Mukamel, X-ray sum frequency diffraction for direct imaging of ultrafast electron dynamics. *Phys. Rev. Lett.* **120**, 243902 (2018).

32. M. Beye, R. Y. Engel, J. O. Schunck, S. Dzialzhytski, G. Brenner, P. S. Miedema, Nonlinear soft x-ray methods on solids with MUSIX—the multi-dimensional spectroscopy and inelastic X-ray scattering endstation. *J. Phys. Condens. Matter* **31**, 014003 (2019).

33. L. Raimondi, C. Svetina, N. Mahne, D. Cocco, A. Abrami, M. De Marco, C. Fava, S. Gerusina, R. Gobessi, F. Capotondi, E. Pedersoli, M. Kiskinova, G. De Ninno, P. Zeitoun, G. Dovillaire, G. Lambert, W. Boutu, H. Merdji, A. Gonzalez, D. Gauthier, M. Zangrando, Microfocusing of the FERMI@Elettra FEL beam with a K–B active optics system: Spot size predictions by application of the WISE code. *Nucl. Instrum. Methods Phys. Res. Sect. A Accel. Spectrometers Detect. Assoc. Equip.* **710**, 131–138 (2013).

34. A. A. Sorokin, Y. Bican, S. Bonfigt, M. Brachmanski, M. Braune, U. F. Jastrow, A. Gottwald, H. Kaser, M. Richter, K. Tiedtke, An X-ray gas monitor for free-electron lasers. *J. Synchrotron Radiat.* **26**, 1092–1100 (2019).

35. T. Kachel, The PM3 beamline at BESSY II. *J. large-scale Res. Facil. JLSRF* **2**, A48 (2016).

36. P. N. Butcher, D. Cotter, *The Elements of Nonlinear Optics* (Cambridge Univ. Press, 1990).

37. A. Milgram, M. P. Givens, Extreme ultraviolet absorption by lithium fluoride. *Phys. Rev.* **125**, 1506–1509 (1962).

38. J. D. Jackson, *Classical Electrodynamics* (John Wiley & Sons Inc., ed. 3, 1998).
39. M. Braune, J. Buck, M. Kuhlmann, S. Grunewald, S. Düsterer, J. Viefhaus, K. Tiedtke, Non-invasive online wavelength measurements at FLASH2 and present benchmark. *J. Synchrotron Radiat.* **25**, 3–15 (2018).

40. B. L. Henke, E. M. Gullikson, J. C. Davis, *X-Ray Interactions With Matter* (U.S. Department of Energy, 1993).

41. B. Henke, E. Gullikson, J. Davis, X-ray interactions: Photoabsorption, scattering, transmission, and reflection at $E = 50$-30,000 eV, $Z = 1$-92. *At. Data Nucl. Data Tables* **54**, 181–342 (1993).