

# X-ray and optical wave mixing

T. E. Glover<sup>1</sup>, D. M. Fritz<sup>2</sup>, M. Cammarata<sup>3</sup>, T. K. Allison<sup>4</sup>, Sinisa Coh<sup>5,6</sup>, J. M. Feldkamp<sup>2</sup>, H. Lemke<sup>2</sup>, D. Zhu<sup>2</sup>, Y. Feng<sup>2</sup>, R. N. Coffee<sup>2</sup>, M. Fuchs<sup>7</sup>, S. Ghimire<sup>7</sup>, J. Chen<sup>7,8</sup>, S. Shwartz<sup>8</sup>, D. A. Reis<sup>7,8,9</sup>, S. E. Harris<sup>8,10</sup> & J. B. Hastings<sup>2</sup>

**Light–matter interactions are ubiquitous, and underpin a wide range of basic research fields and applied technologies. Although optical interactions have been intensively studied, their microscopic details are often poorly understood and have so far not been directly measurable. X-ray and optical wave mixing was proposed nearly half a century ago as an atomic-scale probe of optical interactions but has not yet been observed owing to a lack of sufficiently intense X-ray sources. Here we use an X-ray laser to demonstrate X-ray and optical sum-frequency generation. The underlying nonlinearity is a reciprocal-space probe of the optically induced charges and associated microscopic fields that arise in an illuminated material. To within the experimental errors, the measured efficiency is consistent with first-principles calculations of microscopic optical polarization in diamond. The ability to probe optical interactions on the atomic scale offers new opportunities in both basic and applied areas of science.**

Light–matter interactions have advanced our understanding of atoms, molecules and materials, and are also central to a number of areas of applied science. Although optical interactions have received a great deal of study, the microscopic details of how light manipulates matter are poorly understood in many circumstances. A material's optical response is complex, being determined by coupled many-body interactions that vary on the scale of atoms rather than on the scale of a long-wavelength applied field. Data are needed to combat this complexity, and so far it has not been possible to probe the microscopic details of light–matter interactions.

X-ray and optical wave mixing, specifically sum-frequency generation (SFG), was proposed nearly half a century ago as an atomic-scale probe of light–matter interactions<sup>1,2</sup>. The process is, in essence, optically modulated X-ray diffraction: X-rays inelastically scatter from optically induced charge oscillations and probe optically polarized charge in direct analogy to how standard X-ray diffraction probes ground-state charge. Furthermore, the optically induced microscopic field is determined because it is closely related to the induced charge<sup>3–6</sup>. So far it has not been possible to measure these two quantities directly. X-ray and optical wave mixing has frequently been discussed<sup>1,2,4,7–12</sup>, but it has not yet been demonstrated owing to a lack of sufficiently intense X-ray sources. More generally, although there have been theoretical studies of nonlinear X-ray scattering<sup>13–18</sup>, experimental observations have largely been confined to the spontaneous processes of X-ray parametric down-conversion<sup>19–23</sup> and resonant inelastic X-ray scattering<sup>24,25</sup>.

X-ray free-electron lasers offer unprecedented brightness and new scientific opportunities<sup>26</sup>. Here we use an X-ray laser to demonstrate X-ray/optical SFG through the nonlinear interaction of the two fields in single-crystal diamond. Optically modulated X-ray diffraction from the (111) planes generates a sum-frequency (X-ray plus optical) pulse. The measured conversion efficiency ( $3 \times 10^{-7}$ ) determines the (111) Fourier component of the optically induced charge and associated microscopic field that arise in the illuminated sample. To within experimental errors of  $\sim 40\%$ , the measured charge density is consistent with first-principles calculations of microscopic optical polarization in diamond. The ability to measure atomic-scale charges and fields induced by light should contribute to a better

understanding of materials and create new ways to study photo-triggered dynamics.

## X-ray and optical wave mixing

X-ray and optical wave mixing is an atomic-scale probe of optical interactions: X-rays provide atomic spatial resolution and light makes it possible selectively to probe optically polarized valence charge<sup>1,2</sup>. Sum-frequency radiation is produced when two applied fields simultaneously drive a coherent electronic response; the second field must polarize charge before the polarization due to the first field decays. For X-ray/optical SFG, the simultaneously polarized charge is equal to optically polarized valence charge because only this charge has significant polarizability for both the optical and X-ray fields. Tightly bound core electrons can only be polarized by the X-ray radiation. More generally, as the 'optical' wavelength is varied through the visible to the extreme-ultraviolet (EUV) and soft-X-ray regimes, the polarized charge corresponds to different charge components in a material. Therefore, various charge components can be selectively probed by adjusting the 'optical' wavelength. The SFG technique can, for instance, be extended to probe the full valence charge distribution by mixing X-rays with EUV radiation of a frequency high enough that all valence electrons respond uniformly as free electrons<sup>8,20,23</sup> (but low enough that the polarizability of tightly bound core charge is negligible).

X-ray/optical SFG is a parametric scattering process analogous to standard X-ray diffraction: kinematics are determined by energy and momentum conservation, and the generation of an SFG field is described by the wave equation. In direct analogy to standard X-ray crystallography, inelastically scattered sum-frequency X-rays probe a specific Fourier (that is, reciprocal-space) component of the charge density. Specifically, given an optical wavevector  $k_o$  and reciprocal lattice vector  $G$ , X-ray/optical SFG measures the  $(Q = k_o + G)$ th Fourier component of the optically induced change,  $\delta\rho_o(Q)$ , to the valence charge density.

X-ray/optical SFG, and the closely related process of X-ray/optical difference-frequency generation, probes the linear optical susceptibility on a microscopic length scale. Higher-order X-ray/optical mixing

<sup>1</sup>Advanced Light Source Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA. <sup>2</sup>Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA. <sup>3</sup>Institut de Physique de Rennes, UMR 6251 UR1-CNRS, University Rennes 1, 35042 Rennes Cedex, France. <sup>4</sup>JILA, National Institute of Standards and Technology and University of Colorado, Boulder, Colorado 80309, USA. <sup>5</sup>Department of Physics, University of California, Berkeley, California 94720, USA. <sup>6</sup>Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA. <sup>7</sup>PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA. <sup>8</sup>Department of Applied Physics, Stanford University, Stanford, California 94305, USA. <sup>9</sup>Department of Photon Science, Stanford University, Stanford, California 94305, USA. <sup>10</sup>Department of Electrical Engineering, Stanford University, Stanford, California 94305, USA.

processes can probe nonlinear optical susceptibilities. X-rays, for instance, could scatter from optically induced charge oscillating at twice the optical frequency and thereby be modified by two units of the optical photon energy; this would make it possible to study the atomic-scale details of optical second-harmonic generation.

### Observation of X-ray/optical SFG

We choose diamond as the material in which to demonstrate X-ray/optical SFG: its macroscopic optical<sup>27</sup> and microscopic structural<sup>28</sup> properties are well known and estimates exist for the X-ray/optical SFG efficiency in diamond, although these estimates differ by a factor of  $\sim 100$  (refs 1, 9, 11). An X-ray pulse (8,000 eV,  $\sim 80$  fs) and an optical pulse (1.55 eV,  $\sim 2$  ps,  $\sim 10^{10}$  W cm<sup>-2</sup>) simultaneously illuminate a diamond sample slightly detuned from the optimum orientation for elastic Laue geometry diffraction from the (111) planes (Fig. 1a). Scattered X-rays are wavelength resolved using a Si(220) crystal. The combination of sample detuning and wavelength discrimination reduced the intensity of elastically scattered (background) light reaching our detector by seven to eight orders of magnitude relative to optimum elastic diffraction conditions.

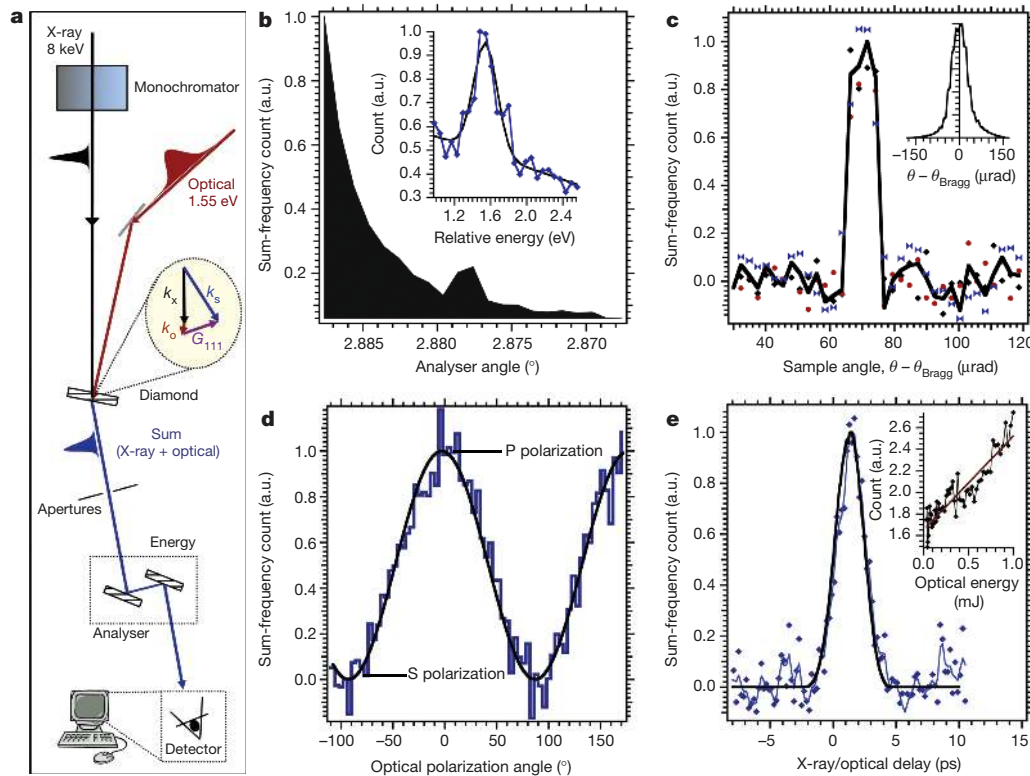
An SFG signal was detected at the expected sample and analyser angles. The signal was observed to depend on the simultaneous presence of X-ray and optical beams, and on optimization we obtained a signal rate of  $\sim 4,000$  detected photons per second. An energy analyser scan (Fig. 1b) confirms a detected photon energy equal to the sum of the input X-ray and optical photon energies and indicates a rocking-curve width ( $17 \pm 2$   $\mu$ rad) in excellent agreement with the intrinsic analyser rocking-curve width ( $\sim 17$   $\mu$ rad). This indicates that the SFG beam is spectrally narrow and well collimated compared with the

energy spread ( $\sim 310$  meV) and angle spread ( $\sim 17$   $\mu$ rad) transmitted by the analyser (called the analyser acceptance). Simulations discussed below are in agreement with this observation.

The analyser was fixed in position and the variation of SFG power with sample angle was measured (Fig. 1c). The signal is sharply peaked at the angle satisfying energy and momentum conservation, and the measured rocking-curve width ( $8.1 \pm 0.7$   $\mu$ rad) is equal, to within the errors, to half the measured analyser width ( $17 \pm 2$   $\mu$ rad). A sample rotation of  $\delta\theta$  causes a  $2\delta\theta$  rotation of the output beam, which indicates that the sample rocking-curve width is set by the limited energy and angle acceptance of the analyser. This observation supports the above conclusion obtained from consideration of the analyser rocking curve (Fig. 1b), namely that the SFG beam is narrow in energy and angle compared with the analyser acceptance. These observations place a lower limit of  $\sim 8$   $\mu$ rad on the SFG rocking-curve width because the SFG intensity is constant over an angular range ( $\sim 8$   $\mu$ rad) limited by the finite analyser acceptance. Simulations discussed below predict an SFG rocking-curve width of 20  $\mu$ rad.

Figure 1d shows how the SFG signal varies with rotation of the optical polarization vector. We expect the efficiency to vary as  $(\epsilon_o \cdot G_{111})^2$ , where  $\epsilon_o$  is the optical polarization vector and  $G_{111}$  is the (111) lattice vector. This scaling reflects the quadratic dependence of SFG efficiency on the linearly induced optical charge, which in turn varies as  $\epsilon_o \cdot G_{111}$ . The SFG signal exhibits the expected dependence: it is maximized when  $\epsilon_o$  is in the scattering plane and it is zero when  $\epsilon_o$  is normal to the scattering plane.

The SFG efficiency was determined by measuring the incident X-ray pulse energy (photons per pulse) and, under both elastic Laue and SFG conditions, the outgoing X-ray pulse energy. The measured



**Figure 1 | X-ray/optical SFG experiment.** **a**, Experimental layout for generation of X-ray (8-keV) and optical (1.55-eV) SFG in diamond. a.u., arbitrary units. **b**, SFG signal versus energy analyser angle. Inset, energy relative to 8 keV. The black line is a Gaussian fit ( $310 \pm 35$  meV,  $17 \pm 2$   $\mu$ rad full-width at half-maximum). The SFG energy exceeds the X-ray energy by one optical photon. **c**, SFG signal versus diamond-sample angle: average of three data scans (width,  $\sim 8$   $\mu$ rad; black line) and individual scans (markers). Energy and momentum conservation is satisfied at  $\theta - \theta_{\text{Bragg}} \approx 70$   $\mu$ rad. Inset, sample rocking curve for elastic diffraction (width,  $\sim 65$   $\mu$ rad)

(measured, blue; expected variation, black) versus angle of optical polarization vector ( $\epsilon_o$ ). The signal is maximum when  $\epsilon_o$  is in the diffraction plane ( $0^\circ$ ) and is zero when  $\epsilon_o$  is normal to the diffraction plane ( $\pm 90^\circ$ ). **e**, SFG signal versus X-ray/optical time delay (raw data, blue markers; one-point-smoothed data, blue curve). Black cross-correlation curve (2.5-ps full-width at half-maximum): solution of wave equation for an 80-fs X-ray pulse and a 1.7-ps optical pulse. Inset, SFG signal versus optical intensity. The red line is a fit to a linear dependence on optical intensity.

efficiency is  $3 \times 10^{-7}$  and the estimated uncertainty is a multiplicative factor of two. The SFG signal strength is a bilinear function of the input beam intensities, varying as the product of the optical and input X-ray intensities. Because the efficiency is defined as the number of SFG photons per input X-ray photon, it is independent of input X-ray intensity but is linearly dependent on optical intensity.

Finally, an X-ray/optical cross-correlation is demonstrated. To within errors of  $\sim 50\%$ , the SFG signal is observed to vary linearly with optical intensity (Fig. 1e, inset). The measured variation in the SFG signal with X-ray/optical relative time delay indicates a cross-correlation width of  $\sim 2.5$  ps (Fig. 1e). By solving the wave equation, we compute the SFG intensity as a function of relative time delay to determine that the measured cross-correlation is reproduced by a simulation with an 80-fs X-ray pulse and a 1.7-ps optical pulse, the second of which is consistent with the experimental optical pulse duration ( $2 \pm 0.5$  ps). The simulated cross-correlation is also shown in Fig. 1e. The cross-correlation width is set by two factors: the duration of the (long) optical pulse and the fact that the X-ray and optical pulses move through the material at different speeds and in different directions.

### Wave equation model

The generation of a sum-frequency electric field is described by the time- and space-dependent wave equation. The slowly-varying-envelope approximation leads to the following equation relating the sum-frequency field ( $E_s$ ) and bilinear current ( $J_{NL}$ ) envelopes (Supplementary Information, section 3):

$$\cos(\theta_s) \frac{dE_s}{dz} + \sin(\theta_s) \frac{dE_s}{dx} + \frac{1}{c} \frac{dE_s}{dt} + \beta E_s = -\frac{2\pi}{c} J_{NL} \quad (1)$$

The  $z$  and  $x$  axes are respectively the inward-facing surface normal and an arbitrary line parallel to the sample surface,  $\beta$  is the X-ray absorption coefficient and  $\theta_s$  is the angle between the  $z$  axis and the sum-frequency wavevector.

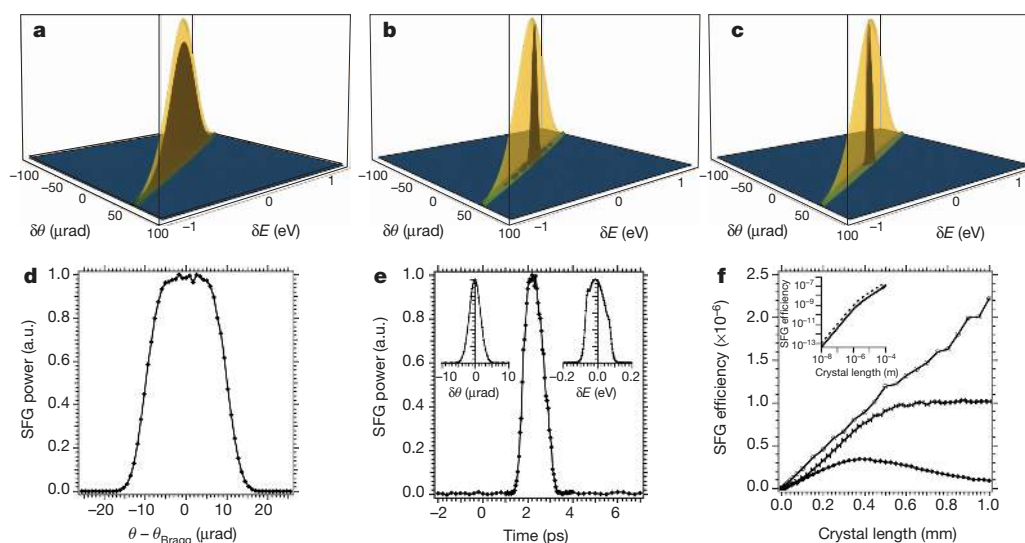
X-rays see diamond as a periodic collection of free electrons ( $h\nu_x \gg h\nu_{\text{binding}}$ , where  $h\nu_x$  is the X-ray photon energy and  $h\nu_{\text{binding}}$  is the electron binding energy;  $h$  is Planck's constant), and the bilinear current, the source of  $E_s$ , is written as a charge times a velocity<sup>29</sup>. We find that the dominant current is the 'Doppler' current

(Supplementary Information, section 4), which represents inelastic scatter as X-rays ( $E_x$ ) impart a first-order velocity to an optically induced charge density ( $\delta\rho_o$ ):

$$J_{NL}(k_{\text{sum}} = Q + k_x, \omega_{\text{sum}} = \omega_o + \omega_x) = \frac{e}{im\omega_x} \delta\rho_o(Q, \omega_o) \varepsilon_s \bullet E_x(k_x, \omega_x) \quad (2)$$

In equation (2),  $\varepsilon_s$  is the sum-frequency polarization vector,  $e$  and  $m$  are respectively the electron charge and mass,  $k_x$  and  $\omega_x$  are respectively the X-ray wavevector and frequency, and  $\delta\rho_o(Q, \omega_o)$  is the Fourier component of the optically induced charge oscillating with spatial wavevector  $Q = k_o + G_{111}$  and optical frequency  $\omega_o$ ; it is induced by, and is therefore a function of, the external applied optical field,  $E_{\text{light}}$ . The input pulses  $E_x$  and  $E_{\text{light}}$  are modelled as Gaussians in space and time with linear chirp parameters determined by their angle–energy spread. With  $J_{NL}$  as given in equation (2) as the source term, we solve the equation obtained by taking a two-dimensional Fourier transform of equation (1).

The power distributions in angle–energy space for the calculated SFG and the driving bilinear current power distributions are shown in Fig. 2a–c for crystal lengths of 1, 10 and 500  $\mu\text{m}$  (the last of which corresponds to our sample). The induced current, which is proportional to the space-time product of the input beams, has an angle–energy power distribution determined by convolution of the Fourier-space input-beam profiles. The angle–energy width of the bilinear current ( $\sim 4$   $\mu\text{rad}$ ,  $\sim 1$  eV) is determined primarily by the angle–energy width of the input X-ray beam; its energy spread (1 eV) is large compared with that of the optical beam ( $< 0.1$  eV), and its transverse wavevector spread is approximately twice that of the optical beam. The angle–energy width of the weakly scattered SFG beam is a fraction of the bilinear current width. In direct analogy with conventional weak X-ray scattering, this fraction is determined by the effective crystal length and is less than one for frequency conversion over a long enough crystal. Figure 2a shows that for crystal lengths less than  $\sim 1$   $\mu\text{m}$ , the current SFG process accepts the full angle–energy width of the bilinear current. Figure 2b, c shows that the SFG angular width is not reduced for crystal lengths up to 500  $\mu\text{m}$  but that the energy width is reduced, to  $\sim 140$  meV at 500  $\mu\text{m}$ .



**Figure 2 | Wave equation simulations.** All quoted widths are full-widths at half-maximum. **a–c**, SFG power distribution (brown) in angle–energy space for sample thicknesses of 1  $\mu\text{m}$  (**a**), 10  $\mu\text{m}$  (**b**) and 500  $\mu\text{m}$  (our sample; **c**). Deviations  $\delta\theta$  and  $\delta E$  from the central SFG angle and energy are plotted. The respective widths are 3.7  $\mu\text{rad}$  and 960 meV (**a**), 3.7  $\mu\text{rad}$  and 210 meV (**b**), and 3.6  $\mu\text{rad}$  and 140 meV (**c**). The driving bilinear current is also shown (3.7  $\mu\text{rad}$  and 1 eV; gold). **d**, SFG power versus deviation from the optimum sample angle,

for a 500- $\mu\text{m}$  crystal. The rocking-curve width is 20  $\mu\text{rad}$ . **e**, SFG pulse duration ( $\sim 1$  ps), angle spread ( $\sim 4$   $\mu\text{rad}$ , left inset) and energy spread ( $\sim 140$  meV, right inset), for a 500- $\mu\text{m}$  crystal. **f**, SFG power versus crystal length with X-ray absorption (diamonds), without absorption for a 1-ps optical pulse (bowties) and without absorption for a long (200-ps) optical pulse (circles). Inset, log-scale plot. The dashed line represents the data for the long optical pulse. The other two cases (solid lines) are indistinguishable.

The calculated SFG rocking-curve width, temporal width and efficiency variation with crystal length are shown in Figs 2d–f. The rocking-curve width (20  $\mu\text{rad}$ ; Fig. 2d) is consistent with the experimentally determined lower limit ( $\sim 8 \mu\text{rad}$ ) and, as with conventional weak X-ray diffraction, is determined by both the effective crystal length and the angle–energy spread of the input beams. The SFG temporal width ( $\sim 1$  ps; Fig. 2e) is larger than the product ( $\sim 80$  fs) of perfectly overlapped X-ray ( $\sim 80$  fs) and optical ( $\sim 2$  ps) pulses because these two pulses move through the crystal at different speeds and in different directions. With regard to dependence on crystal length, the SFG intensity decreases for crystals longer than  $\sim 400 \mu\text{m}$  owing to X-ray absorption (Fig. 2f). In the absence of absorption, the X-ray/optical velocity mismatch combined with our non-collinear geometry (different beam directions) leads to saturation of SFG efficiency as a function of crystal length (Fig. 2f) because the pulses eventually separate from one another. Without the velocity mismatch, the increase of efficiency with crystal length no longer saturates (Fig. 2f). The efficiency also improves with increased input-beam collimation, monochromaticity or both, to  $\sim 10^{-3}$  for X-ray energy and angle widths of 0.1 meV and  $1 \mu\text{rad}$  and optical energy and angle widths of 10 meV and 1 mrad, respectively. This assumes a 500- $\mu\text{m}$ -long crystal and neglects loss due to absorption.

Equations (1) and (2) show that the fundamental unknown specifying  $E_y/E_x$  and, therefore, the SFG efficiency is the optically induced charge  $\delta\rho_o(Q)$ ; it is determined by requiring that the wave equation model reproduce the measured SFG efficiency ( $3 \times 10^{-7}$ ), a requirement satisfied by  $\delta\rho_o(Q) \approx 0.84 \times 10^{-4}$  electrons per cubic ångström ( $e^- \text{Å}^{-3}$ ). Furthermore, we define a nonlinear susceptibility ( $\chi_{\text{NL}}$ ) such that  $J_{\text{NL}}$  is written as a product of  $E_x$ ,  $E_{\text{light}}$  and  $\chi_{\text{NL}}$  rather than in terms of  $\delta\rho_o(Q)$ . The measured efficiency corresponds to a nonlinear susceptibility of  $\chi_{\text{NL}}(\omega_o + \omega_x, G_{111}) \approx 1.6 \times 10^{-14}$  e.s.u. Finally, the measured quantity  $\delta\rho_o(Q)$  determines the microscopic field  $\delta E_o(Q)$  associated with this charge because the two are related by Gauss's law<sup>3–6</sup>. Here  $\delta E_o(Q)$  is the  $Q$ th Fourier component of the microscopic field arising in diamond as a result of the application of the external field  $E_{\text{light}}$  (refs 3–6). We find that  $|\delta E_o(Q = k_o + G_{111})| \approx 0.47$  in units of the macroscopic internal optical field and  $\sim 0.18$  in units of the unscreened external optical field. The uncertainty in  $\delta\rho_o(Q)$ ,  $\chi_{\text{NL}}(G_{111})$  and  $\delta E_o(Q)$  is  $\sim 40\%$ , determined by the estimated uncertainty of a factor of two in the measured efficiency. The connections between the efficiency, induced charge, nonlinear susceptibility and induced microscopic field are discussed in Supplementary Information, section 2.

### Optically polarized valence charge

Associating optically polarized charge with the charge components of interest in a material is important for X-ray/optical SFG pump–probe applications. Here we consider atomic-scale optical polarization in diamond. Models that assign all optical polarizability to covalent bond charge, here termed bond charge models, have had success describing the macroscopic optical response of covalent semiconductors<sup>30,31</sup>. To test whether this idea can be extended to describe atomic-scale polarizability, we compare measured charge densities with those calculated from first principles. We find that the Fourier-space induced charge computed using density functional theory<sup>32,33</sup> ( $\delta\rho_o(G_{111}) = 1.07 \times 10^{-4} e^- \text{Å}^{-3}$ ; Methods; see also <http://www.quantum-espresso.org>) is, to within the  $\sim 40\%$  experimental error, consistent with the measured charge density ( $\sim 0.84 \times 10^{-4} e^- \text{Å}^{-3}$ ).

A real-space picture of the induced charge is required to assess whether light primarily polarizes bond charge. Such a real-space reconstruction is beyond the scope of the experiments reported here. Instead, we compute the real-space induced charge distribution using density functional theory. The computed ground-state valence charge density (Fig. 3a, d) shows that the covalent bond is characterized by two charge accumulation peaks, one on each side of the bond midpoint, a feature confirmed by X-ray scattering data<sup>28</sup>. The corresponding induced charge calculation (Fig. 3b, e) shows that optical

polarization is predominantly expressed at the charge accumulation peaks of the covalent bond; this can be seen by comparing the positions of peak bond charge density and peak optically induced charge density (Fig. 3c, f). We find that the induced charge varies linearly with optical field strength and, for the optical field strength of the current experiment, corresponds to a 0.2% modification to the charge density at the charge accumulation peak. The density functional theory calculations therefore support a view that light predominantly perturbs chemical bonds in the lattice. We note that EUV radiation ( $90 \pm 30$  eV) predominantly polarizes charge at the bond midpoint rather than at the charge accumulation peaks<sup>23</sup>.

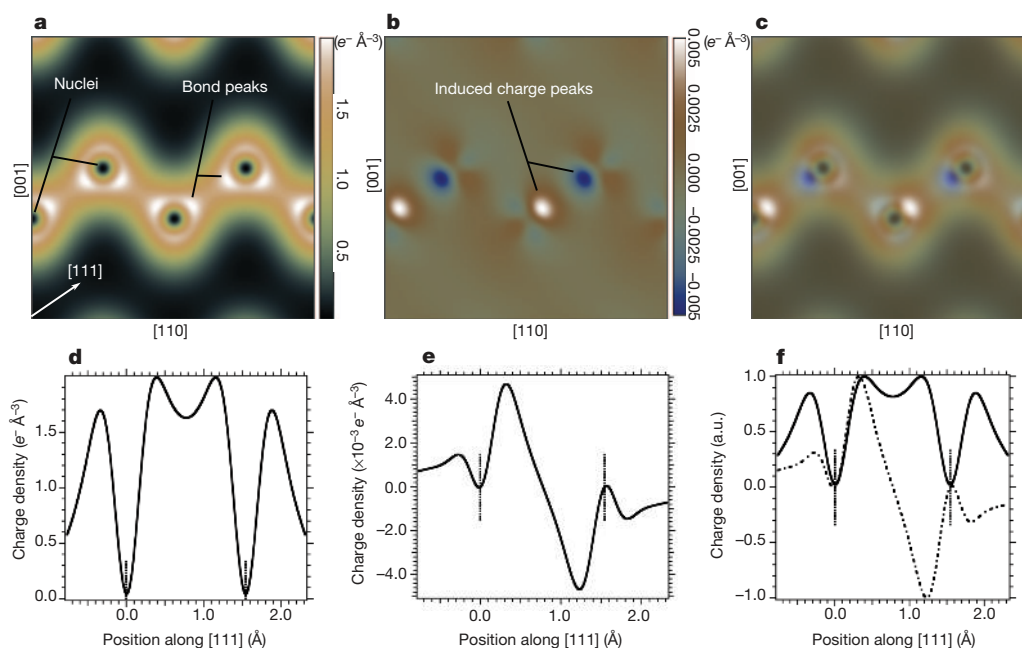
Finally, we have constructed a simple semi-empirical bond charge model in the spirit of ref. 1 (Supplementary Information, section 1) and find that to within our estimated measurement uncertainty, a multiplicative factor of  $\sim 1.4$ , the bond charge model predicts a charge density ( $\sim 1.3 \times 10^{-4} e^- \text{Å}^{-3}$ ) in reasonably good agreement with the measured charge density ( $\sim 0.84 \times 10^{-4} e^- \text{Å}^{-3}$ ). The bond charge model uses measured data: the macroscopic optical response and the microscopic bond charge distribution. An assessment of this model is therefore primarily an assessment of the assumption that optical polarizability resides in the bond charge. Although confirmation in the form of an experimental real-space reconstruction of the induced charge is required, reasonable agreement between measured densities and those predicted by the bond charge model lends further support to the identification of bond charge as the optically polarizable charge.

### Probing dynamics with X-ray wave mixing

Ultrafast X-ray diffraction (UXD) is a well-established technique that has made important contributions to advancing our understanding of molecular and material dynamics<sup>34–38</sup>. The method uses time-delayed X-ray pulses to follow ionic cores after sudden excitation, often by an optical pulse. Ionic cores are followed because compact charge about the nucleus, or ‘core’ charge, typically dominates the electron density in a material. Importantly, information on the chemically relevant valence charge is typically not obtained in experiments using ultrafast X-ray diffraction. X-ray wave mixing provides a way to probe the valence charge density in a material. It can be used to probe both the initial perturbation of a light-driven process as well as the subsequent valence charge dynamics. We first consider the initial perturbation.

The perturbation initiating a light-driven process is often poorly understood and, so far, has not been directly measurable. An X-ray pulse can accompany a perturbing optical pulse to probe the initial valence charge distortion directly by means of X-ray/optical SFG. A real-space reconstruction of the induced charge can, in principle, be obtained by measuring multiple Fourier components and using crystallographic phasing methods<sup>39,40</sup>. As with conventional crystallography, the achievable spatial resolution is, through Bragg's law, set by the scattering angle<sup>40</sup>. A less challenging method is to measure a small set of SFG Fourier amplitudes to distinguish between competing model descriptions of the initial perturbation. For instance, magneto-optical Kerr measurements (S. Roy *et al.*, manuscript in preparation) suggest that optical radiation perturbs the helical spin structure in antiferromagnetic dysprosium thin films. However, the underlying mechanism is unclear: light might directly couple to localized spin-aligned  $f$  electrons or the direct coupling may instead be to delocalized metallic electrons. By measuring a small number of X-ray/optical SFG Fourier amplitudes, it should be possible to determine the degree to which the initial optical excitation is localized and therefore to distinguish between these possibilities.

Beyond probing initial optical perturbations, the evolution of valence charge in a material can be probed with a time-delayed pulse pair: an X-ray/optical pair to probe optically responsive charge or an X-ray/EUV pair to probe a significantly larger fraction of the valence charge<sup>8,20,23</sup>. Unfavourable frequency scaling of the electronic polarizability suggests that the efficiency of X-ray/EUV SFG is significantly



**Figure 3 | Density functional theory calculations of real-space valence charge density in diamond.** **a**, Ground-state charge density (colour scale) showing the covalent bond charge accumulation peaks. **b**, Induced charge density produced by a constant field ( $2.7 \times 10^8 \text{ V m}^{-1}$ ) in the [111] direction. **c**, Induced charge image (**b**) overlaid on the unperturbed charge image (**a**), demonstrating that optical polarization is primarily found at the charge

accumulation peaks. **d–f**, Charge density along the [111] direction and through the bond peaks for **a–c**, respectively. The bond peaks (0.39 and 1.16 Å; **d**) and induced charge peaks (0.32 and 1.23 Å; **e**) are evident; **f** shows normalized densities for both the ground-state (solid) and the induced (dashed) charge distributions.

lower than that of X-ray/optical SFG. We calculate that the bilinear current (the square root of the efficiency) for X-ray (8,000 eV)/EUV (100 eV) SFG is  $\sim 5,000$  times smaller than that for X-ray (8,000 eV)/optical (1.55 eV) SFG (Supplementary Information, section 4). Although X-ray/EUV SFG could in principle be used to construct time-dependent valence charge density maps, the expected low efficiency may make this an application to which future light sources are better suited. For experiments in which the significantly lower signal rate is not acceptable, X-ray/optical SFG can be used to probe a selected portion of the valence charge.

A material's optical polarizability is not uniformly distributed across the valence charge and, rather than probing the full valence charge distribution, X-ray/optical SFG selectively probes the optically polarizable component. To the extent that the optically polarizable charge can, through measurement and theory, be correctly associated with charge components of interest in a material, it should be possible to obtain novel dynamical information. For instance, assuming, as suggested above, that the optically polarizable charge in diamond is bond charge, chemical bond dynamics can be studied by measuring the time evolution of select X-ray/optical SFG Bragg peaks. Ultrafast X-ray diffraction experiments using the temporal behaviour of conventional Bragg peaks have offered insight into, among other things, charge ordering dynamics in complex materials<sup>35</sup>, coherent atomic motion associated with both phonon<sup>36</sup> and phonon–polariton<sup>37</sup> propagation, and bond softening in optically excited materials<sup>38</sup>. Analogous experiments that probe valence charge should provide additional insight. For instance, the coupling between ionic cores and chemical bonds could be studied: induced coherent ionic-core oscillations will induce chemical bond oscillations that may differ from the core oscillations in any combination of phase, amplitude and frequency. Similarly, bond delocalization or breaking would have a clear signature in the evolution of selected X-ray/optical SFG Bragg peaks.

Finally, to comment on the viability of X-ray/optical SFG at existing synchrotrons, we estimate that if the same experimental apparatus (including a 1-kHz optical laser) were used in conjunction with a

third-generation synchrotron such as the Advanced Photon Source, it would take  $\sim 4,000$  times longer to obtain data with the same statistics (Supplementary Information, section 6). By using high-repetition-rate (1-MHz) optical lasers, it may be possible to approach the count rate of the current experiment at a third-generation synchrotron (Supplementary Information, section 6).

## Conclusion

We have demonstrated X-ray/optical SFG, a new tool for probing light–matter interactions on the atomic scale. To within experimental errors of  $\sim 40\%$ , the measured conversion efficiency ( $3 \times 10^{-7}$ ) is consistent with first-principles calculations of atomic-scale optical polarization in diamond. This measurement, in combination with *ab initio* simulations, supports the extension to atomic length scales of the long-held supposition that light selectively polarizes chemical bonds in covalent semiconductors. This conclusion is tentative and must be confirmed by an experimental real-space reconstruction of the optically polarized charge.

More generally, X-ray wave mixing creates new opportunities for probing matter. X-ray/optical SFG provides access to two closely related and previously inaccessible quantities: the induced charges and the associated microscopic fields that arise when light illuminates a material. The ability to measure optically induced microscopic fields provides novel data for benchmarking condensed-matter theories. Similarly, X-ray/optical SFG and the closely related X-ray/EUV SFG process create new opportunities to study dynamics by directly probing valence charge on atomic time and length scales.

## METHODS SUMMARY

**Experiment.** Experiments were performed at the Linac Coherent Light Source<sup>26</sup> (LCLS). The 8-keV LCLS beam ( $\sim 1.7 \mu\text{rad}$ ,  $\sim 20$ -eV full-width at half-maximum,  $\sim 80$  fs) passed through a Si(111) monochromator and was directed to a (100)-surface-cut diamond sample oriented for Laue geometry diffraction from the (111) planes. X-ray/optical SFG was observed using 800-nm optical pulses ( $\sim 1.5 \times 10^{10} \text{ W cm}^{-2}$ ) stretched to a duration ( $\sim 2$  ps) long compared with the X-ray/optical timing jitter ( $\sim 200$  fs). Switching from elastic diffraction to SFG was accomplished by rotating the diamond sample by  $\sim 70 \mu\text{rad}$ , moving the

analyser crystal to the expected SFG beam position and then rotating the analyser to increase the central pass energy by 1.55 eV ( $h\nu_{\text{optical}}$ , where  $\nu_{\text{optical}}$  is the optical frequency). Scattered X-rays were wavelength-resolved with a Si(220) channel-cut crystal.

**Variability in wave equation predictions.** Input beams are modelled as linearly chirped Gaussians with spatial and temporal chirp parameters adjusted to match angle and energy widths:  $\sim 4.1 \pm 1$  mrad and  $68 \pm 10$  meV for the optical beam and  $\sim 1.7 \pm 1$   $\mu$ rad and  $1 \pm 0.1$  eV for the X-ray beam. The SFG efficiency varies by less than 2% for the stated variations in all parameters except for X-ray energy. We estimate an uncertainty of 10% in the X-ray bandwidth ( $1 \pm 0.1$  eV) and determine that this corresponds to an uncertainty of 10% in the predicted SFG efficiency, which is small compared with the uncertainty (of a factor of two) in the measured SFG efficiency. We considered two X-ray pulse models: an  $\sim 80$ -fs (actual duration) pulse with a 1-eV bandwidth accounted for by a linear frequency chirp, and a transform-limited ( $\sim 2$ -fs) pulse with a 1-eV bandwidth. We find that the SFG efficiency and pulse duration are insensitive to these choices, varying by less than 2%.

**Full Methods** and any associated references are available in the online version of the paper.

Received 14 February; accepted 18 June 2012.

- Freund, I. & Levine, B. F. Optically modulated X-ray diffraction. *Phys. Rev. Lett.* **25**, 1241–1245 (1970).
- Eisenberger, P. M. & McCall, S. L. Mixing of X-ray and optical photons. *Phys. Rev. A* **3**, 1145–1151 (1971).
- Jackson, J. D. *Classical Electrodynamics* (Wiley, 1975).
- Arya, K. & Jha, S. S. Microscopic optical fields and mixing coefficients of x-ray and optical frequencies in solids. *Pramana* **2**, 116–125 (1974).
- Adler, S. L. Quantum theory of the dielectric constant in real solids. *Phys. Rev.* **126**, 413–420 (1962).
- Pine, A. S. Self-consistent-field theory of linear and nonlinear crystalline dielectrics including local-field effects. *Phys. Rev.* **139**, A901–A911 (1965).
- Woo, J. W. F. & Jha, S. S. Inelastic scattering of x rays from optically induced charge-density oscillations. *Phys. Rev. B* **6**, 4081–4082 (1972).
- Freund, I. Nonlinear X-ray diffraction: determination of valence electron charge distributions. *Chem. Phys. Lett.* **12**, 583–588 (1972).
- Van Vechten, J. A., & Martin, R. M. Calculation of local effective fields: optical spectrum of diamond. *Phys. Rev. Lett.* **28**, 446–449 (1972).
- Freund, I. & Levine, B. F. Surface effects in the nonlinear interaction of X-ray and optical fields. *Phys. Rev. B* **6**, 3059–3060 (1973).
- Arya, K. & Jha, S. S. Microscopic optical fields in diamond and germanium: molecular-orbital approach. *Phys. Rev. B* **10**, 4485–4487 (1974).
- Johnson, D. L. Local field effects and the dielectric response matrix of insulators: A model. *Phys. Rev. B* **9**, 4475–4484 (1974).
- Schweigert, I. V. & Mukamel, S. Coherent ultrafast core-hole correlation spectroscopy: X-ray analogues of multidimensional NMR. *Phys. Rev. Lett.* **99**, 163001 (2007).
- Tanaka, S. & Mukamel, S. Probing exciton dynamics using Raman resonances in femtosecond X-ray four-wave mixing. *Phys. Rev. A* **67**, 033818 (2003).
- Nazarkin, A., Podorov, S., Uschmann, I., Forster, E. & Sauerbrey, R. Nonlinear optics in the angstrom regime: hard-X-ray frequency doubling in perfect crystals. *Phys. Rev. A* **67**, 041804(R) (2003).
- Tanaka, S. & Mukamel, S. Coherent X-ray Raman spectroscopy: a nonlinear local probe for electronic excitations. *Phys. Rev. Lett.* **89**, 043001 (2002).
- Hudis, E., Shkolnikov, P. L. & Kaplan, A. E. X-ray stimulated Raman scattering in Li and He. *Appl. Phys. Lett.* **64**, 818–820 (1994).
- Freund, I. & Levine, B. F. Parametric conversion of X rays. *Phys. Rev. Lett.* **23**, 854–857 (1969).
- Eisenberger, P. & McCall, S. L. X-ray parametric conversion. *Phys. Rev. Lett.* **26**, 684–688 (1971).
- Danino, H. & Freund, I. Parametric down conversion of X rays into the extreme ultraviolet. *Phys. Rev. Lett.* **46**, 1127–1130 (1981).
- Yoda, Y., Suzuki, T., Zhang, X. W., Hirano, K. & Kikuta, S. X-ray parametric scattering by a diamond crystal. *J. Synchrotron Radiat.* **5**, 980–982 (1998).
- Adams, B. *et al.* Parametric down conversion of X-ray photons. *J. Synchrotron Radiat.* **7**, 81–88 (2000).
- Tamasaku, K., Sawada, K., Nishibori, E. & Ishikawa, T. Visualizing the local optical response to extreme-ultraviolet radiation with a resolution of  $\lambda/380$ . *Nature Phys.* **7**, 705–708 (2011).
- Platzman, P. M. & Isaacs, E. D. Resonant inelastic X-ray scattering. *Phys. Rev. B* **57**, 11107–11114 (1998).
- Kotani, A. & Shin, S. Resonant inelastic X-ray scattering spectra for electrons in solids. *Rev. Mod. Phys.* **73**, 203–246 (2001).
- Emma, P. *et al.* First lasing and operation of an ångstrom-wavelength free-electron laser. *Nature Photon.* **4**, 641–647 (2010).
- Palik, E. D. (ed.) *Handbook of Optical Constants of Solids* 313–334 (Academic, 1998).
- Spackman, M. A. The electron distribution in diamond: a comparison between experiment and theory. *Acta Crystallogr. A* **47**, 420–427 (1991).
- Shen, Y. R. *The Principles of Nonlinear Optics* 5–40 (Wiley, 1984).
- Phillips, J. C. Covalent bond in crystals. I. Elements of a structural theory. *Phys. Rev.* **166**, 832–838 (1968).
- Levine, B. F. Electrodynamic bond-charge calculation of nonlinear optical susceptibilities. *Phys. Rev. Lett.* **22**, 787–790 (1969).
- Giannozzi, P. *et al.* Quantum Espresso: a modular and open-source software project for quantum simulations of materials. *J. Phys. Condens. Matter* **21**, 395502 (2009).
- Souza, I., Iniguez, J. & Vanderbilt, D. First principles approach to insulators in finite electric fields. *Phys. Rev. Lett.* **89**, 117602 (2002).
- Ihee, H. *et al.* Ultrafast X-ray diffraction of transient molecular structures in solution. *Science* **309**, 1223–1227 (2005).
- Möhr-Vorobeva, E. *et al.* Nonthermal melting of a charge density wave in TiSe<sub>2</sub>. *Phys. Rev. Lett.* **107**, 036403 (2011).
- Lindenberg, A. M. *et al.* Time-resolved X-ray diffraction from coherent phonons during a laser-induced phase transition. *Phys. Rev. Lett.* **84**, 111–114 (2000).
- Cavalleri, A. *et al.* Tracking the motion of charges in a terahertz light field by femtosecond X-ray diffraction. *Nature* **442**, 664–666 (2006).
- Fritz, D. M. *et al.* Ultrafast bond softening in bismuth: mapping a solid's interatomic potential with X-rays. *Science* **315**, 633–636 (2007).
- Wu, J. S., Spence, J. C. H., O'Keefe, M. & Groy, T. L. Application of a modified Oszlanyi and Suto ab initio charge-flipping algorithm to experimental data. *Acta Crystallogr. A* **60**, 326–330 (2004).
- Coppens, P. *X-Ray Charge Densities and Chemical Bonding* (Oxford Univ. Press, 1997).

**Supplementary Information** is available in the online version of the paper.

**Acknowledgements** We thank J. D. Jackson, D. Vanderbilt, and J. C. H. Spence for commenting on various aspects of this work. T.E.G. was supported by the Office of Science, Office of Basic Energy Sciences, of the US Department of Energy under contract no. DE-AC02-05CH11231. The work of S.E.H. and S.S. was supported by the US Air Force Office of Scientific Research and the US Army Research Office. D.A.R. and S.G. were supported as part of the AMOS programme within the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, US Department of Energy. Portions of this research were carried out at the LCLS at SLAC National Accelerator Laboratory. LCLS is an Office of Science User Facility operated for the US Department of Energy Office of Science by Stanford University. Preliminary experiments were performed at the Advanced Light Source at Lawrence Berkeley National Laboratory.

**Author Contributions** T.E.G. and J.B.H. had the idea for the x-ray/optical SFG project. D.M.F., T.E.G., J.B.H., M.C., T.K.A., J.M.F. and D.A.R. contributed to the experiment design. D.M.F., M.C., H.L., D.Z. and R.N.C. were responsible for the X-ray pump-probe instrument and the optical laser. D.M.F., M.C., T.E.G., J.B.H., H.L., D.Z., T.K.A., J.M.F., Y.F., R.N.C., D.A.R., S.S., M.F., S.G. and J.C. collected data. S.E.H., S.S., T.E.G. and T.K.A. contributed to the wave equation calculations. Data analysis was done by T.E.G., H.L. and J.M.F. Construction of the bond charge model was done by T.E.G. Density functional theory calculations were done by S.C. T.E.G. wrote the manuscript. All authors contributed to the work presented here and to the final paper.

**Author Information** Reprints and permissions information is available at [www.nature.com/reprints](http://www.nature.com/reprints). The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to T.E.G. ([teglower@lbl.gov](mailto:teglower@lbl.gov)).

## METHODS

**Experiment.** Experiments were performed at the LCLS<sup>26</sup>, an X-ray free-electron laser that provided an 8-keV, 60-Hz beam with angle and energy spreads of respectively  $\sim 1.7 \mu\text{rad}$  and  $\sim 20 \text{ eV}$  (full-widths at half-maximum). The  $\sim 80\text{-fs}$  pulse (full-width at half-maximum) contained  $\sim 5 \times 10^{10}$  photons. Complications from spectral jitter were mitigated by converting spectral fluctuations to intensity fluctuations: X-rays were passed through a two-bounce Si(111) monochromator ( $\sim 1\text{-eV}$  bandpass) and a non-destructive Compton scattering diagnostic recorded the shot-by-shot beam intensity to normalize intensity fluctuations. Monochromatic X-rays ( $\sim 1.7 \mu\text{rad}$ ,  $1 \text{ eV}$ ) were directed to a (100)-surface-cut diamond sample oriented for 8-keV, (111) Laue geometry diffraction. A Si(220) channel-cut crystal was used to energy-resolve detected X-rays. X-ray/optical SFG was observed using 800-nm optical pulses ( $1.5 \times 10^{10} \text{ W cm}^{-2}$ ) stretched to a duration ( $\sim 2 \text{ ps}$ ) long compared with the X-ray/optical timing jitter ( $\sim 200 \text{ fs}$ ). X-ray/optical overlap was achieved by maximizing the reduction in X-ray diffraction from an optically perturbed Bi sample.

Switching from elastic diffraction to SFG was accomplished by first rotating the diamond sample by  $\delta\phi_{111} \approx 70 \mu\text{rad}$  (less grazing). A two-theta arm then rotated the analyser to the expected SFG beam position,  $\sim 370 \mu\text{rad}$  relative to the elastically scattered beam position before the diamond rotation. Finally, the central pass energy of the analyser was increased (such that the optical photon energy was  $h\nu_{\text{optical}} = 1.55 \text{ eV}$ ) by rotating the crystal itself ( $\delta\phi_{220} \approx 85 \mu\text{rad}$ ). The sample and analyser detunings, each  $\sim 10$  rocking-curve half-widths, reduced the intensity of elastically scattered (background) light reaching the detector by seven to eight orders of magnitude relative to optimized elastic scattering conditions ( $\delta\phi_{111} = \delta\phi_{220} = 0$ ). We did not make use of the  $\sim 500\text{-}\mu\text{rad}$  angular separation between the elastic and SFG beams.

The X-ray flux reaching our detector was  $\sim 3 \times 10^7$  photons per pulse under optimized elastic diffraction conditions, which is less than the initial  $\sim 5 \times 10^{10}$  photons per pulse due to loss associated with both absorption and five crystal reflections (two Si(111), the diamond sample and two Si(220)). The SFG flux reaching our detector was  $\sim 65$  photons per pulse.

**Variability in wave equation predictions.** Input beams were modelled as linearly chirped Gaussians with spatial and temporal chirp parameters adjusted to match

the corresponding angle and energy widths: The optical beam had an energy spread of  $68 \text{ meV}$  and an in-vacuum angle spread of  $\sim 4.1 \text{ mrad}$ . A linear frequency chirp stretched the optical pulse to a duration ( $\sim 2 \text{ ps}$ ) long compared with the X-ray/optical timing jitter ( $\sim 200 \text{ fs}$ ). The X-ray angle spread ( $\sim 1.7 \mu\text{rad}$ ) was set by the LCLS divergence whereas the energy spread ( $\sim 1 \text{ eV}$ ) was set by the Si(111) monochromator. Two X-ray pulse models were considered: one with a pulse duration equal to the actual LCLS duration ( $\sim 80 \text{ fs}$ ) and a  $1\text{-eV}$  bandwidth accounted for by a linear frequency chirp, and one with a transform-limited pulse with a duration ( $\sim 2 \text{ fs}$ ) determined by the  $1\text{-eV}$  bandwidth. We find that the SFG efficiency and pulse duration are insensitive to these choices; each varies by less than 2%. Insensitivity of efficiency to the specific duration of the (short) X-ray pulse might be expected because for either pulse duration the X-ray pulse is short compared with the optical pulse and therefore sees the same optical field strength. Similarly, pulse duration insensitivity seems reasonable because the X-ray and optical pulses move through the crystal at different speeds; this causes the relative X-ray/optical time delay to vary linearly across the crystal. The magnitude of this 'time shift' ( $> 1 \text{ ps}$ ) is large compared with either X-ray pulse duration considered ( $80$  or  $2 \text{ fs}$ ). The actual LCLS pulse is probably a random distribution of transform-limited spikes within a  $\sim 80\text{-fs}$  temporal envelope.

Finally, the predicted efficiency depends on the degree to which the input beams are collimated and/or monochromatic; here we consider how much the predicted efficiency varies owing to uncertainty in the angle–energy spread of the input beams. We estimate the uncertainties in the X-ray energy, laser wavelength, X-ray angle and laser angle 'widths' to be  $\pm 0.1 \text{ eV}$ ,  $\pm 10 \text{ meV}$ ,  $\pm 1 \mu\text{rad}$  and  $\pm 1 \text{ mrad}$ , respectively. The variation in the predicted SFG efficiency is less than 2% for the stated variations in all parameters except for X-ray energy. The variation in efficiency with X-ray energy spread is approximately linear. The bandwidth of the X-ray beam should be known to good precision because it is set by the Si(111) monochromator acceptance. We estimate an uncertainty of  $\sim 10\%$  in the X-ray bandwidth ( $1 \pm 0.1 \text{ eV}$ ), which corresponds to a variation of  $\sim 10\%$  in the predicted efficiency. This uncertainty is small compared with the uncertainty in the measured SFG efficiency, which is a factor of two as determined by variability in the measured X-ray/SFG pulse energy.