Probing materials using x-ray and optical wave mixing

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A new scattering technique using high-intensity x-rays can directly probe the way in which light manipulates electrons in a material on an atomic scale.

Light-matter interactions have advanced our understanding of atoms, molecules, and materials. They are also central to a number of applied areas including vision, solar energy conversion, optoelectronics, and photonics. In spite of their widespread importance, relatively little is definitively known about macroscopic optical interactions because it has not been possible to directly measure the optical response of a material on an atomic length scale. Although light is uniform on a microscopic scale, a material—and therefore its induced polarization—varies on the scale of atoms. Coupled atomic-scale interactions between polarization sites determine the actual field that arises in an illuminated material. Understanding the magnitude, and in some cases even the direction, of the force exerted on charges in a material is challenging. With the trend toward device miniaturization and an increasing interest in quantum materials, our understanding of microscopic optical interactions and new, direct measurement techniques must be developed.

X-rays are routinely used to probe matter on an atomic scale, but they can only be used to visualize the optical rearrangement or charge in a material in some very specialized cases. This limitation arises from the very different frequencies, or photon energies, associated with x-ray versus optical radiation. Optical photon energies are well suited for exciting the weakly bound, chemically relevant valence electrons in a material, but much higher photon energy is necessary to excite the chemically inert ‘core’ electrons held tightly around the nucleus. This enables us to say, to a good approximation, that light interacts exclusively with the valence electrons. However, x-rays have much higher photon energy and interact with both core and valence electrons. Since there are usually many more core than valence electrons in a material, conventional x-ray scattering is typically dominated by scatter from core electrons. Except for very specialized situations in which scatter from core electrons cancels that from others, the valence electron signal is typically lost in the statistical noise of the much larger core signal, rendering it unmeasurable. We have recently demonstrated a new technique that distinguishes valence from core scattered x-rays, thereby providing a means to directly measure microscopic optical interactions.

X-ray and optical sum frequency generation (x/o SFG) is a technique that was first proposed nearly a half century ago by scientists at Bell Laboratories. Light illuminates a material and vibrates some of the electrons at the optical frequency, polarizing a component of the valence charge. X-rays can inelastically scatter from the optically driven charge oscillations, thereby either increasing (sum frequency generation) or...
decreasing (difference frequency generation) the x-ray photon energy by an amount equal to the optical photon energy. Until recently, x-ray sources were too weak to observe this effect. However, new possibilities are created by state-of-the-art x-ray free-electron lasers.

Our experiments\(^3\) were performed at the world’s first hard x-ray free-electron laser, the Linac Coherent Light Source\(^4\) at the SLAC National Accelerator Laboratory. We simultaneously illuminated a diamond crystal with two femtosecond-duration laser pulses, one x-ray and one optical, resulting in a combination of core-scattered and energy-modified valence-scattered x-rays being diffracted from the (111) planes in diamond. The scattered x-rays are detected by a photodiode after being energy filtered by reflection from a silicon crystal. Figure 1 shows how the photodiode signal varies as we alter the ‘pass energy’ of the silicon crystal. A prominent peak is observed for x-rays with energy \(\sim 1.5\text{eV} (h\nu_{\text{optical}})\) higher than the input x-ray energy, which confirms that we have detected sum-frequency x-rays. The measured efficiency (here \(3 \times 10^{-7}\)) uniquely determines the (111) Fourier component of the optically induced charge in diamond. The measured charge density is consistent with first principles calculations of microscopic optical polarization in diamond.\(^3\) These measurements and supporting calculations validate the long-held supposition that light primarily interacts with the bond charge in covalent semiconductors.

In summary, direct measurement of the atomic-scale details surrounding the way in which light manipulates charge in a material is now possible using high-intensity x-ray lasers. We have demonstrated this capability by measuring a single x/o SFG Fourier component in diamond, a heavily studied and well understood material. Given the complexity inherent in such problems, new tools such as the one demonstrated here will play an important role in the development of new devices with functionality controlled by ultrafast light pulses, such as those found in the fields of superconductivity and quantum electronics. This technique could also enable further study into the way in which light manipulates magnetic order in correlated electron materials. The next stage of our experiments will pursue two frontiers: visualizing optical charge manipulation in real space by measuring a number of Fourier components and using phase recovery techniques appropriate to crystallography, and applying x/o SFG to the study of advanced materials.

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References