Microscopic electron dynamics in nonlinear optical response of solids

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We investigate the microscopic properties of the nonlinear optical response of crystalline solids within Floquet theory, and demonstrate that optically-induced microscopic charge distributions display complex spatial structure and nontrivial properties. Their spatial symmetry and temporal behavior are governed by crystal symmetries. We find that even when a macroscopic optical response of a crystal is forbidden, the microscopic optical response can, in fact, be nonzero. In such a case, the optically-induced charge redistribution can be considerable, even though the corresponding Fourier component of the time-dependent dipole moment per unit cell vanishes. We develop a method that makes it possible to completely reconstruct the microscopic optically-induced charge distributions by means of subcycle-resolved x-ray-optical wave mixing. We also show how, within this framework, the direction of the instantaneous microscopic optically-induced electron current flow can be revealed.

I. INTRODUCTION

The optical response of crystals has been extensively investigated for more than a hundred years. Such studies have predominantly concentrated on the macroscopic optical response of a crystal, since it determines typical experimentally-detectable observables, such as harmonic generation. The macroscopic optical response of a crystal is mostly results from an induced dipole moment. Typically, the radiation power produced by the oscillating dipole moment dominates over the radiation power produced by higher-order moments in the optical regime [1], and the macroscopic polarization in a dielectric material results from the induced dipole moment [2]. For this reason, it is customary to relate linear and nonlinear optical response to the induction of dipole moments.

In recent years, laser-driven electron dynamics has gained considerable attention due to remarkable achievements in the field of nonlinear optics including the generation of high-harmonics (HHG) in solids [3, 4], optical-field-induced currents in dielectrics [5], manipulation of electric properties of a dielectric with the electric field of light [6], control of coherent Bloch oscillations [7, 8], subcycle terahertz nonlinear optical effects [9] and coherent control of currents in semiconductors using synthesized optical waveforms [10]. These achievements motivated theoretical and experimental studies to understand the mechanisms behind these phenomena [11–25].

At the same time, due to the significant progress of attosecond science, sub-femtosecond x-ray pulses can now be generated [26–31]. Such ultrashort x-ray pulses enable real-time measurements of electron dynamics with sub-nanometer spatial resolution. In this article, we develop a method that employs ultrafast nonresonant x-ray scattering to probe in real time charge and electron current distributions within a unit cell of a crystal during the interaction with an optical field. This method provides access to the microscopic nonlinear optical response of band-gap crystals. We show that, on an atomic scale, a µth-order optically-induced charge distribution leading to a µth-order macroscopic polarization is much more complex than can be captured by focusing exclusively on dipole moments. The widely-used concept that optically-induced charge separation merely gives rise to a dipole moment fails on an atomic scale. Induced charge distributions have a rich structure and various symmetry features. Even when the induction of a macroscopic polarization is forbidden, charges still rearrange within a unit cell and electron currents are induced.

The idea to probe optically-induced charge distributions with x-ray scattering signal from a laser-driven crystal, i.e., with an x-ray-optical wave mixing signal, dates back to the 1970s [32, 33]. Since its experimental realization at the x-ray free-electron laser facility Linac Coherent Light Source (LCLS), where the microscopic linear optical response of a diamond crystal was detected as a sum-frequency signal in x-ray diffraction [34], x-ray-optical wave mixing techniques have again moved into the focus of research [35–38]. In this article, we analyzed the spatial symmetry and temporal behavior of microscopic optically-induced charge and electron-current distributions, and their connection to the time and momentum dependence of subcycle-resolved x-ray-optical wave-mixing signals. Based on this analysis, we develop a method to reconstruct microscopic linear and nonlinear charge rearrangements and the direction of electron current flow induced by optical excitation, by means of subcycle-resolved x-ray-optical wave mixing.

We describe the interaction of the driving field with a crystal within the framework of the Floquet formal-
ism [39]. This is a powerful theoretical concept that has been applied to diverse phenomena, such as quantum engineering of novel states of matter aided by a periodic excitation [40–48] or nonperturbative processes driven by an intense laser field [15, 49–53]. Specifically, we employ the Floquet-Bloch framework, which is capable of a nonperturbative material-specific description of laser-dressed spatially periodic structures [49, 50, 54]. Properties of Floquet-Bloch systems have mainly been analyzed with a focus on HHG [15, 50, 54–57] or band-structure modification by light [49, 57–59]. Here, we apply the Floquet-Bloch formalism as an elegant and insightful framework to calculate laser-induced charge and electron current distributions in real space and real time.

In Ref. 38, we developed a general theoretical framework to describe the interaction of general Floquet systems with an x-ray pulse. It is based on the framework of quantum electrodynamics (QED) and the density matrix formalism [60], which is necessary for a correct description of the interaction of an ultrashort light pulse with a nonstationary electronic system [61, 62]. Here, we employ the tools developed in that study to show which insights x rays can reveal about the microscopic optical response.

As we will demonstrate, understanding the information encoded in the subcycle-resolved x-ray-optical wave mixing signal relies on the analysis of the spatial symmetry and temporal dependence of optically-induced charge distributions and the electron current density. Thus, we analyze in Sec. II properties of the microscopic optical response within the Floquet-Bloch formalism. In Sec. III, we calculate the microscopic optical response of two band-gap materials, the insulator MgO and the semiconductor GaAs driven by an intense optical field. By studying these two prototypical materials, we cover two types of crystals, one with inversion symmetry, MgO, and one without inversion symmetry, GaAs. In Sec. IV, we develop a method to measure the microscopic optical response by means of ultrafast x-ray-optical wave mixing.

II. MICROSCOPIC OPTICALLY-INDUCED CHARGE AND ELECTRON-CURRENT DISTRIBUTIONS

The Floquet formalism implies that the electric field of the driving field is temporally periodic. It has been shown in Refs. 55 and 63 that this approximation is already justified for a strong-field optical field with a duration comprising several tens of optical cycles. Throughout this paper, we consider a laser-dressed crystal in a state that is characterized by a single Floquet state. To justify this approximation, it should be assured that the driving field is not too strong to bring the laser-dressed system into a superposition of several Floquet states [64]. The applicability of these approximations can be verified with the radiation spectrum generated by the system through the driving field. If they do not hold, the radiation spectrum will have additional peaks besides the harmonic ones. Thus, our study applies to the regime in which each generated radiation peak can be clearly assigned to an integer multiple of the driving-laser frequency. This regime of light-matter interaction includes conventional linear- and nonlinear-optics experiments, in which a single-mode electromagnetic field perturbatively interacts with an optical crystal. It also concerns modern experiments in which a crystal nonperturbatively interacts with an ultrashort light pulse, but the radiation spectrum still consists of harmonic peaks [3, 4, 7, 8, 21].

We briefly review the classical limit of the quantized Floquet-Bloch formalism that we use to describe the nonperturbative interaction of an optical electromagnetic field with a band-gap crystal [39, 49, 50, 52, 54]. The quantized representation is necessary to introduce the interaction of a laser-dressed crystal with an ultrashort x-ray pulse within the QED framework in the next step [38]. The Hamiltonian of a laser-dressed crystal is given by

\[ \hat{H}_{\text{el-em}} = \hat{H}_{\text{el}} + \hat{H}_{\text{int}} + \hat{H}_{\text{em}}, \]
\[ \hat{H}_{\text{el}} = \int d^3 r \hat{\psi}^\dagger(r) \left[ \frac{\mathbf{p}^2}{2} + V_c(r) \right] \hat{\psi}(r), \]
\[ \hat{H}_{\text{int}} = \alpha \int d^3 r \hat{\psi}^\dagger(r) \left( \hat{A}_{\text{em}}(r) \cdot \mathbf{p} \right) \hat{\psi}(r). \]

Here, \( \hat{H}_{\text{el}} \) is the mean-field Hamiltonian of the unperturbed crystal with one-body eigenstates \( |\varphi_{m\mathbf{k}}\rangle \), where \( \mathbf{k} \) is the Bloch wave vector and \( m \) is the band and spin index. \( V_c(r) = V_c(r + \mathbf{R}) \) is a space-periodic crystal field potential, \( \mathbf{R} \) is a lattice vector. According to the Bloch theorem [65], the corresponding one-body wave function of \( |\varphi_{m\mathbf{k}}\rangle \) has the form \( \varphi_{m\mathbf{k}}(r) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{m\mathbf{k}}(r) \), where \( u_{m\mathbf{k}}(r) = u_{m\mathbf{k}}(r + \mathbf{R}) \) is a space-periodic function. \( \mathbf{p} \) is the canonical momentum of an electron, \( \hat{\psi}^\dagger \hat{\psi} \) is the electron creation (annihilation) field operator. \( \hat{H}_{\text{em}} \) is the Hamiltonian of the electromagnetic field, and \( \hat{H}_{\text{int}} \) the interaction Hamiltonian between the electromagnetic field and the electronic system, which we describe within the dipole approximation. \( \hat{A}_{\text{em}}(\mathbf{k}) \) creates (annihilates) a photon with wave vector \( \mathbf{k} \) and polarization \( s \). We assume that only the \( \mathbf{k}_0, s_0 \) mode with a corresponding polarization vector \( \mathbf{e}_0 \) and the energy \( \omega = |\mathbf{k}_0| c \), where \( c \) is the speed of light, is occupied in the driving electromagnetic field, and that the state of the field is described by a single-mode coherent state \( |\alpha, t\rangle \). \( \hat{A}_{\text{em}}(r) \) is the vector potential operator of the electromagnetic field, and \( \alpha \) is the fine-structure constant. We neglect the \( \hat{A}_{\text{em}}^2 \) contribution for the optical field. We use atomic units for these and the following expressions.

Since the state of the electromagnetic field \( |\alpha, t\rangle \) is unaffected by the interaction with the electronic system by assumption, the one-body solution of the time-dependent Schrödinger equation \( i\hbar \frac{d}{dt} |\psi_{\mathbf{k}, t}\rangle = \hat{H}_{\text{el-em}} |\psi_{\mathbf{k}, t}\rangle \) can be represented as \( |\psi_{\mathbf{k}, t}\rangle = |\phi_{\mathbf{k}, t}\rangle |\alpha, t\rangle \) with the corre-
sponding electronic one-body Floquet-Bloch wave function \([39, 50, 54]\)

\[
\phi_{i,k}^{(1)}(r,t) = \sum_{m,\mu} c_{m,k,\mu}^{i} e^{i \mu \omega t} \varphi_{m,k}(r),
\]

where \(\mu\) is an integer and the \(c_{m,k,\mu}^{i}\) are expansion coefficients.

A. Electron-density amplitudes

The electron density of the laser-dressed system evolves in time as \([38]\)

\[
\rho(r,t) = \sum_{\mu} e^{i \mu \omega t} \tilde{\rho}_{\mu}(r)
\]

with \(\mu\)-th-order density amplitudes

\[
\tilde{\rho}_{\mu}(r) = \int_{BZ} \frac{d^{3}k}{V_{uc}} \sum_{m,m',i,\mu'} c_{m',k,\mu'+\mu}^{i} \tilde{u}_{m,k}(r) u_{m,k}(r),
\]

where \(V_{uc}\) is the volume of a unit cell, \(i\) denotes the index of occupied one-body Floquet-Bloch states and the integration is over the Brillouin zone. The \(\mu\)-th-order density amplitudes can be connected to properties of the \(\mu\)-th-order macroscopic optical response. For example, the polarization is determined by the time-dependent electron density

\[
P(t) \propto \int d^{3}r \rho(r,t),
\]

and the \(\mu\)-th-order component of the polarization is determined by the \(\mu\)-th-order density amplitude

\[
\tilde{P}^{(\mu)}(\mu \omega) \propto e^{i \mu \omega t} \int d^{3}r \tilde{\rho}_{\mu}(r).
\]

Thus, the amplitudes \(\tilde{\rho}_{\mu}(r)\) are optically-induced charge distributions that give rise to a \(\mu\)-th-order macroscopic optical response.

Our connection of the density amplitudes to the macroscopic polarization is consistent with the classical derivation of macroscopic polarization \([66, 67]\). The conventional expansion of the polarization in orders of \(\omega\), \(P = P^{(1)}(\omega) + P^{(2)}(2\omega) + P^{(3)}(3\omega) + \cdots\), also holds within the Floquet formalism. But in the nonperturbative regime, \(\mu\)-th-order components should not scale as the \(\mu\)-th power of the electric-field amplitude.

The volume integral of a \(\mu\)-th-order density amplitude over a unit cell is given by

\[
\int d^{3}r \tilde{\rho}_{\mu}(r) = \int_{BZ} \frac{d^{3}k}{V_{uc}} \sum_{m,m',i,\mu'} c_{m',k,\mu'+\mu}^{i} \varphi_{m,k}(r) \delta_{m,m'},
\]

We now apply the orthogonality of the expansion coefficients \(\sum_{m,\mu'} c_{m,k,\mu'}^{i} \delta_{m,\mu'} = \delta_{m,\mu} \). Thus, the volume integral of the time-independent part of the electron density gives the number of electrons

\[
\int d^{3}r \hat{\rho}_{0}(r) = N_{el},
\]

reproducing the volume integral of the unperturbed electron density. The volume integral of the density amplitudes of a nonzero order that enter in the time-dependent part of \(\rho(r,t)\) is zero

\[
\int d^{3}r \tilde{\rho}_{\mu \neq 0}(r) = 0.
\]

These relations indicate that the interaction of a crystal with light leads to a dynamical redistribution of charges, which has positive and negative regions relative to the field-free electron density. These positive and negative regions coherently oscillate, and cancel each other when volume integrated. The positively charged regions are due to electron holes in valence bands and negatively charge regions are due to electrons in conduction bands.

B. Time-reversal symmetry

In the following, we will show that the time-reversal symmetry of a crystal determines the temporal behavior of the laser-driven electron oscillations. The derivations below are applied to a general situation, in which the crystal is not necessarily invariant under inversion symmetry in real space. First, let us consider how time-reversal symmetry influences the properties of the Floquet-Bloch functions. For a Bloch function \(\varphi_{m,k}(r)\) of an unperturbed crystal that obeys time-reversal symmetry, it is valid that \(\varphi_{m,k}(r) = \varphi_{m,-k}(r)\) \([65]\). Similarly to the proof of this property, we show below that for a one-body electronic wave function of a laser-dressed crystal with time-reversal symmetry, it is true that

\[
\phi_{i,k}^{el}(r,t) = \phi_{i,-k}^{el}(r,T/2 - t),
\]

where \(T = 2\pi/\omega\) is the period of the driving electromagnetic field.

Applying to the time-dependent Schrödinger equation

\[
i \frac{d}{dt} \phi_{i,k}^{el}(t) = \hat{H}_{el} \phi_{i,k}^{el}(t) + i \phi_{i,k}^{el}(t) \frac{d|\alpha, t\rangle}{dt}
\]

\[
= (\hat{H}_{el} + \hat{H}_{int} + \hat{H}_{em})(\phi_{i,k}^{el}(t)|\alpha, t\rangle
\]

that the coherent state \(|\alpha, t\rangle\) obeys \(i \alpha|\alpha, t\rangle/dt = \hat{H}_{em}|\alpha, t\rangle\) and multiplying Eq. (14) by \(|\alpha, t\rangle\), we obtain

\[
i \frac{d}{dt} \phi_{i,k}^{el}(t) = \hat{H}_{el}\phi_{i,k}^{el}(t) + \langle\alpha, t|\hat{H}_{int}|\alpha, t\rangle \phi_{i,k}^{el}(t).
\]

The matrix element \(|\alpha, t|\hat{H}_{int}|\alpha, t\rangle\) gives the interaction Hamiltonian in the classical limit \(\hat{H}_{cl}^{int}(t) = \)
\[ \pi \int d^3r \hat{\psi}^\dagger(r) \mathbf{A}_e(r_0, t) \cdot \mathbf{p} \hat{\psi}(r), \] where \( \mathbf{A}_e(r_0, t) = (c/\omega)E_{em}(r_0) \cos(\omega t) \) is \( E_{em}(r_0) \) being the amplitude of the electric field. Since we apply the dipole approximation, we ignored the spatial variation of the vector potential and the electric-field amplitude, and substituted the position of the crystal \( r_0 \) for \( r \) in \( \mathbf{A}_e(r_0, t) \) and \( E_{em}(r_0) \).

Thus, the one-body electronic wave function obeys
\[ i \frac{\partial \phi_{i,k}^{cl}(r, t)}{\partial t} = [\hat{H}_{el} + \hat{H}_{int}^{cl}(t)] \phi_{i,k}^{cl}(r, t). \] (16)

In order to prove Eq. (13), we take the complex conjugate of Eq. (16) resulting in
\[ -i \frac{\partial \phi_{i,k}^{el}(r, t)}{\partial t} = [\hat{H}_{el} - \hat{H}_{int}^{el}(t)] \phi_{i,k}^{el}(r, t). \] (17)

Here we applied that \( \hat{H}_{int}^{el}(t) = -\hat{H}_{int}^{el}(t) \) and \( \hat{H}_{el}^{\dagger} = \hat{H}_{el} \) for crystals with the time-reversal symmetry [65]. We now rewrite the above expression for the time \( T/2 - t \) taking into account that \( \mathbf{A}_em(r_0, T/2 - t) = -\mathbf{A}_em(r_0, t) \):\[ i \frac{\partial \phi_{i,k}^{el}(r, T/2 - t)}{\partial t} = [\hat{H}_{el} + \hat{H}_{int}^{el}(t)] \phi_{i,k}^{el}(r, T/2 - t). \]

Thus, we obtain that if the wave function \( \phi_{i,k}^{el}(r, t) \) is a solution of the time-dependent Schrödinger equation, then \( \phi_{i,k}^{el}(r, T/2 - t) \) is also a solution. Since \( \phi_{i,k}^{el}(r + R, t) = e^{i k_R} \phi_{i,k}^{el}(r, t) \), it must be valid that \( \phi_{i,k}^{el}(r + R, T/2 - t) = e^{-i k_R} \phi_{i,k}^{el}(r, T/2 - t) \). Thus, the solution \( \phi_{i,k}^{el}(r, T/2 - t) \) is the solution at the Bloch vector \( -k \), and we have proven Eq. (13). Eq. (13) leads to a connection between the corresponding expansion coefficients of Floquet-Bloch functions [cf. Eq. (5)], \[ e^{i \mu k} = (-1)^{\mu} c_{m-k}^{cl}, \] (19)

which follows from the phase relation \( e^{i \mu \omega t} = (-1)^{\mu} e^{-i \omega (T/2 - t)} \).

1. Density amplitudes

We now make use of Eq. (19) and the property of the Bloch functions of crystals with time-reversal symmetry that \( u_{mk}(r) = u_{m-k}^{*}(r) \) [65] to connect terms with opposite \( k \) in the integral for \( \tilde{\rho}_\mu(r) \) in Eq. (7). This allows us to reduce the integration over the Brillouin zone to half of the Brillouin zone (BHZ). \[ \tilde{\rho}_\mu(r) = \int_{\text{BHZ}} \frac{d^3k}{V_{uc}} \sum_{m,m',\mu',\mu} e^{i m\omega_k} \rho_{m,k,\mu'}^{cl} e^{i m\omega_k} u_{m,k}^{*}(r) u_{m,k}(r) \]

It follows from this relation that even-order density amplitudes \( \tilde{\rho}_{\mu_{\text{even}}}(r) \) are real functions, whereas odd-order density amplitudes \( \tilde{\rho}_{\mu_{\text{odd}}}(r) \) are purely imaginary.

This property has an important consequence for the time dependence of the electron density. To see this, we use Eq. (20) to combine terms with opposite \( \mu \) in the expression for the time-dependent electron density in Eq. (6),

\[ \rho(r,t) = \tilde{\rho}_0(r) - \sum_{m,\mu_{\text{odd}} \geq 1} q_{\mu_{\text{odd}}} \sin(\mu_{\text{odd}} \omega t) + \sum_{\mu_{\text{even}} \geq 2} q_{\mu_{\text{even}}} \cos(\mu_{\text{even}} \omega t). \] (21)

Here, we also used the relation \( \tilde{\rho}_\mu(r) = \tilde{\rho}_{-\mu}(r) \), which can be easily shown independently of the crystal symmetry. In Eq. (21), we redefined the density amplitudes as follows:
\[ q_{\mu_{\text{even}}}(r) = 2 \text{Re}[\tilde{\rho}_{\mu_{\text{even}}}(r)], \] (22)
\[ q_{\mu_{\text{odd}}}(r) = 2 \text{Im}[\tilde{\rho}_{\mu_{\text{odd}}}(r)], \] (23)

which are real functions for both even and odd \( \mu \). This representation of electron density amplitudes is more insightful in comparison to the functions \( \tilde{\rho}_\mu(r) \), since it demonstrates the actual time dependence of the light-induced charge distributions. Throughout the article, we will mainly refer to the density amplitudes defined by the real-valued functions in Eqs. (22) and (23), but will refer to the amplitudes \( \tilde{\rho}_\mu(r) \) in Sec. IV.

Thus, we find that odd-order induced charge distributions oscillate as harmonics in phase with the electric field and even-order induced charge distributions oscillate as harmonics in phase with the vector potential. When the electric field is zero, the absolute values of odd-order density amplitudes are zero and the absolute values of even-order density amplitudes are maximal. When the electric field is maximal, the absolute values of odd-order density amplitudes are maximal and the absolute values of even-order density amplitudes are zero. This property is a consequence of a time-reversal symmetry of the crystal. Broken time-reversal symmetry would lead to a different relation between the phases of induced-charge and electric-field oscillations.
2. Electron current density

We now study how time-reversal symmetry influences the oscillations of the electron current density. Properties of HHG have been investigated using the Floquet-Bloch formalism in several studies [15, 54, 56, 57]. Here, we analyze the electron current density, which is the microscopic property that determines HHG.

The electron current density in the presence of the electromagnetic field is given by [54, 68]

\[
\mathbf{j}(\mathbf{r}, t) = -\rho(\mathbf{r}, t) \mathbf{A}_{\text{em}}(\mathbf{r}_0, t) + \int_{\text{BZ}} \frac{d^3k}{V_{\text{uc}}} \text{Im} \left[ \sum_k \phi_{l,k}^{\text{el}}(\mathbf{r}, t) \nabla \phi_{l,k}^{\text{el}}(\mathbf{r}, t) \right].
\]

(24)

Using the relation between the expansion coefficients of Floquet-Bloch functions at opposite \( \mathbf{k} \) due to the time-reversal symmetry in Eq. (19), we obtain that the electron current density evolves in time as

\[
\mathbf{j}(\mathbf{r}, t) = -\sum_{\mu_{\text{odd}} \geq 1} \mathbf{j}_{\mu_{\text{odd}}} \cos(\mu_{\text{odd}} \omega t) - \sum_{\mu_{\text{even}} \geq 2} \mathbf{j}_{\mu_{\text{even}}} \sin(\mu_{\text{even}} \omega t),
\]

(25)

where

\[
\mathbf{j}_{\mu_{\text{odd}}} = 2 \int_{\text{BZ}} \frac{d^3k}{V_{\text{uc}}} \text{Im} \tilde{\mathbf{j}}_{\mu_{\text{odd}}} + \frac{E_{\text{em}}(\mathbf{r}_0)}{2\omega} \left[ \varrho_{\mu_{\text{odd}}-1} + \varrho_{\mu_{\text{odd}}+1} \right],
\]

(26)

\[
\mathbf{j}_{\mu_{\text{even}}} = 2 \int_{\text{BZ}} \frac{d^3k}{V_{\text{uc}}} \text{Re} \tilde{\mathbf{j}}_{\mu_{\text{even}}} - \frac{E_{\text{em}}(\mathbf{r}_0)}{2\omega} \left[ \varrho_{\mu_{\text{even}}-1} + \varrho_{\mu_{\text{even}}+1} \right]
\]

(27)

with

\[
\tilde{\mathbf{j}}_{\mu_{\text{odd}}} = \sum_{i,m,i',\mu'} c_{m',k,\mu'}^{i*} c_{m,k,\mu} \varphi_{m'k} \nabla \varphi_{m'k} - \varphi_{mk} \nabla \varphi_{mk}
\]

(28)

are real-valued amplitudes of the electron current density. Thus, the electron current density amplitudes oscillate with a phase shifted by \( \pi/2 \) with respect to the oscillations of the charge distributions of the same order. When the absolute value of the \( \mu \)-th order charge oscillation is at a maximum, the \( \mu \)-th order electron current density is zero and vice versa.

Applying the continuity equation

\[
\text{div} \mathbf{j}(\mathbf{r}, t) = -\partial \rho(\mathbf{r}, t)/\partial t = \sum_{\mu_{\text{odd}} \geq 1} \mu_{\text{odd}} \omega \varrho_{\mu_{\text{odd}}} \cos(\mu_{\text{odd}} \omega t) + \sum_{\mu_{\text{even}} \geq 2} \mu_{\text{even}} \omega \varrho_{\mu_{\text{even}}} \sin(\mu_{\text{even}} \omega t),
\]

(29)

we obtain the following relation between the amplitudes of the electron current density and the amplitudes of the electron density:

\[
\text{div} \mathbf{j}_\mu(\mathbf{r}) = -\mu_\omega \varrho_\mu(\mathbf{r}).
\]

(30)

Let us now analyze the connection between the dipole moment of the density amplitudes \( \int d^3r \rho_\mu(\mathbf{r}) \) and the electron-current-density amplitudes:

\[
\int d^3r \rho_\mu(\mathbf{r}) = -\frac{1}{\mu_\omega} \int d^3r \text{div} \mathbf{j}_\mu(\mathbf{r})
\]

(31)

\[
= -\frac{1}{\mu_\omega} \oint r \mathbf{j}_\mu(\mathbf{r}) \cdot d\mathbf{S} + \frac{1}{\mu_\omega} \int d^3r r \mathbf{j}_\mu(\mathbf{r}).
\]

(32)

The second line of Eq. (31) follows from vector-algebra relations for the dipole moment of a divergence. Since the volume integral of the optically-induced charge distributions \( \varrho_{\mu \neq 0} \) is zero, we find

\[
\mu_\omega \int d^3r \varrho_\mu = -\int d^3r \text{div} \mathbf{j}_\mu(\mathbf{r}) = -\oint \mathbf{j}_\mu(\mathbf{r}) \cdot d\mathbf{S} = 0.
\]

Both surface integrals \( \oint \mathbf{j}_\mu(\mathbf{r}) \cdot d\mathbf{S} \) and \( \oint r \mathbf{j}_\mu(\mathbf{r}) \cdot d\mathbf{S} \) can be zero only if the electron current density \( \mathbf{j}_\mu(\mathbf{r}) \) on the boundary of a unit cell is zero. Thus, if this is the case, the \( \mu \)-th order macroscopic polarization is proportional to the volume integral of the \( \mu \)-th order electron-current-density amplitudes.
C. Crystal with inversion symmetry

In this subsection, we assume that the crystal exposed to periodic driving is invariant under inversion symmetry and, consequently, $\hat{H}_{\text{el}}(\mathbf{r}) = \hat{H}_{\text{el}}(-\mathbf{r})$. The interaction Hamiltonian $\hat{H}_{\text{int}}$ is invariant under the transformations $\mathbf{r} \to -\mathbf{r}$ and $t \to t - T/2$. Thus, it follows from the time-dependent Schrödinger equation in Eq. (16) that [56]

$$\frac{d\phi_{i,k}^\text{el}(t)}{dt} = \left[\hat{H}_{\text{el}} + \hat{H}_{\text{int}}(t)\right]\phi_{i,k}^\text{el}(t) + \hat{H}_{\text{int}}(t)\phi_{i,k}^\text{el}(t).$$

(33)

Since $\phi_{i,k}^\text{el}(t) = e^{\text{i}k\mathbf{R}\phi_{i,k}^\text{el}(t)}$, $\phi_{i,k}^\text{el}(t)$ is a solution at $-\mathbf{k}$ and

$$\phi_{i,k}^\text{el}(-\mathbf{r}, t - T/2) = \phi_{i,k}^\text{el}(\mathbf{r}, t).$$

(34)

The Bloch functions of crystals that are invariant under inversion symmetry obey the relation $\varphi_{mk}^\text{el}(\mathbf{r}) = \varphi_{m,k}^\text{el}(-\mathbf{r}) = \varphi_{m,k}^\text{el}(-\mathbf{r})$ [65]. Substitution of the relations between Bloch and Floquet-Bloch functions into the expansion of Floquet-Bloch functions in Eq. (5) gives a relation between the expansion coefficients at opposite $\mathbf{k}$:

$$c_{m,k,\mu} = (-1)^\mu c_{m,-k,\mu}.$$

(35)

Comparing it with the relation between the coefficients due to time-reversal symmetry in Eq. (19), we find that the coefficients $c_{m,k,\mu}$ are real.

Substitution of these properties into the expression for the electron density amplitudes via Bloch functions in Eq. (7) leads to the following connection between complex amplitudes at opposite $\mathbf{r}$

$$\tilde{\rho}_\mu(-\mathbf{r}) = \tilde{\rho}_\mu(\mathbf{r}).$$

(36)

The property of these amplitudes that either their imaginary or real part is zero depending on the parity of $\mu$ determines how they behave under inversion symmetry. The same holds for the real-valued representation of the density amplitudes in Eqs. (22) and (23) that all even-order density amplitudes are invariant under inversion symmetry, whereas all odd-order density amplitudes are opposite under inversion symmetry:

$$\varrho_{\mu\text{even}}(\mathbf{r}) = \varrho_{\mu\text{even}}(-\mathbf{r}),$$

(37)

$$\varrho_{\mu\text{odd}}(\mathbf{r}) = -\varrho_{\mu\text{odd}}(-\mathbf{r}).$$

(38)

Analogously, using that $\varphi_{mk}(-\mathbf{r}) = \varphi_{mk}^*(\mathbf{r})$ [65], $\nabla \cdot \mathbf{r} = -\nabla \mathbf{r}$, and the coefficients $c_{m,k,\mu}$ being real, we obtain the following symmetry properties of the current density amplitudes

$$j_{\mu\text{even}}(\mathbf{r}) = -j_{\mu\text{even}}(-\mathbf{r}),$$

(39)

$$j_{\mu\text{odd}}(\mathbf{r}) = j_{\mu\text{odd}}(-\mathbf{r}).$$

(40)

Since the volume integral of functions that are antisymmetric is zero, the volume integral of the even-order current density amplitudes is zero

$$\int d^3 r j_{\mu\text{even}}(\mathbf{r}) = 0,$$

(41)

which leads to the well-known selection rule that even-order harmonics from crystals invariant under inversion symmetry are forbidden [69].

In this Section, we analyzed microscopic properties of optically-induced charge distributions and the electron current density. The temporal dependence of the light-induced oscillations of the electronic state is determined by time-reversal symmetry. We found that components of the electron density oscillate either in phase with the electric field or in phase with the vector potential depending on the parity of the oscillation order. The inversion symmetry of a crystal results in the inversion symmetry of the $\mu$th-order charge distributions and $\mu$th-order amplitudes of the electron current density. Thereby, their behavior under the transformation $\mathbf{r} \to -\mathbf{r}$ depends on the parity of the order. As an outlook, it is interesting to analyze the consequence of other crystal symmetries on the spatial and temporal properties of optically-induced charge distributions. The Floquet-Bloch formalism is a convenient tool to perform such an analysis.

III. MICROSCOPIC OPTICAL RESPONSE IN BAND-GAP CRYSTALS MgO AND GaAs

A. Computational details

We diagonalize the Floquet-Bloch Hamiltonian as described in Refs. [38, 54]. We calculate the one-body wave functions $\varphi_{mk}$ of the field-free Hamiltonian $\hat{H}_{\text{el}}$ within the density functional theory using the ABINIT software package [70–72] in combination with Troullier-Martins pseudopotentials [73]. The functions $\varphi_{mk}$ of valence bands and conduction bands are calculated on a dense grid of $\mathbf{k}$ points in half of the Brillouin zone. The numbers of blocks of the Floquet-Bloch matrix, $\mathbf{k}$ points, and bands are increased in the computations till convergence of the Fourier components of the electron density amplitudes is reached.

The conduction bands that are necessary to converge the optical response are actually the bands into which electrons are excited by the electromagnetic field with a nonvanishing probability. The number of conduction bands involved in the interaction with the optical field strongly depends on the intensity of the optical field and crystal properties. This number increases with the intensity of the optical field, and is well above ten in the non-perturbative regime. There are several reasons for such a high required number of conduction bands. The first reason is that the higher the intensity of the optical field, the larger is the probability of an off-resonant transition into energetically high conduction bands. For example, a transition from a valence band into a conduction band with an energy difference detuned by 10 eV from the photoenergy of the driving field can contribute to the first harmonic, if the intensity of the optical field is sufficiently high.

The next reason is that the higher the intensity of the
optical field, the larger is the probability of a resonant multiphoton transition. As an example, let us consider the seven-photon absorption process induced by a field with a photon energy of \( \omega = 1.55 \) eV. A transition from a valence band to a conduction band with an energy difference of \( 7\omega = 10.85 \) eV is resonant and should have a dominating contribution to this process. Then, it is crucial to take into account the conduction bands lying at \( \approx 11 \) eV above the outermost valence band for the calculation of the seventh-order optical response. The number of generated harmonics increases with increasing field intensity, and so should increase the number of conduction bands that are necessary to take into account for the calculation of a high harmonic spectrum. Multiphoton transitions also contribute to the optical response at lower orders in the nonperturbative regime. For example, seven-photon absorption combined with six-photon emission can contribute to the first-order response.

### B. Crystal with inversion symmetry, MgO

We first calculate the microscopic optical response of a crystal with inversion symmetry, MgO. We consider driving optical field with an intensity of \( I_{\text{em}} = 2 \times 10^{12} \) W/cm\(^2\), a photon energy of 1.55 eV, and polarization axis \( \epsilon = (0, 0, 1) \). The calculation is performed using a 24 \( \times \) 24 \( \times \) 24 Monkhorst-Pack grid, four valence and sixteen conduction bands, and 81 blocks of the Floquet Hamiltonian, which are necessary to reach convergence. The driving field and the computational parameters are the same as we used to calculate the subcycle-unresolved x-ray-optical wave mixing signal from laser-dressed MgO in Ref. 38. There, we showed that an optical field of \( 2 \times 10^{12} \) W/cm\(^2\) drives electron dynamics in MgO nonperturbatively. For the current computation, we additionally apply the scissors approximation [74] to correct the band gap from the calculated 5.6 eV to the experimental value of 7.8 eV [75], which is necessary to obtain the correct position of inelastic x-ray scattering in the spectrum as shown in Sec. IV.

Figure 1 shows the calculated microscopic response of the MgO crystal depending on the phase of the driving electromagnetic field with the electric field evolving as \( E_{\text{em}} \sin(\omega t) \). A cut of a unit cell centered at the Mg atom is shown. The first column displays the first-order oscillations of the electronic state, i.e., the oscillations of the electron density and the electron current density with frequency \( \omega \) in response to the driving electromagnetic field. As shown in Sec. II B, the first-order oscillations of the electronic state of the laser-driven crystal comprise the oscillations of the electron current density as \(-j_1(r) \cos(\omega t)\) and the oscillations of the electron density as \(-\rho_1 \sin(\omega t)\).

The first-order optically-induced electronic state at \( \omega t = 0 \) is shown in Fig. 1(a). At this phase, the electric field of the optical field is zero, the magnitude of the microscopic first-order electron current is at a maximum, and the first-order electron density is zero. Thus, Fig. 1(a) shows only the first-order electron current density \(-j_1(r)\). The \( \mu \)-th order electron current amplitudes \( j_\mu(r) \) are three-dimensional vector fields that are nonzero at most points within the unit cell. For the purpose of intuitive visual representation, the electron current densities in this and other figures are plotted on a sparse grid and only vectors with magnitudes \(|j_\mu(r)|\) larger than a certain minimum threshold are shown. The magnitudes of \( j_\mu(r) \) are color coded and their values are in atomic units. The minimum threshold for \(|j_\mu(r)|\) in a given plot is the minimum value of the corresponding color box.

The first-order electron current density in Fig. 1(a) points along the driving-field polarization direction, and its magnitude \(|j_\mu(r)|\) has pronounced peaks at the oxygen atoms. The electron current causes the charge to rearrange within the unit cell and, at \( \omega t = \pi/2 \), the first-order electron density \(-\rho_1 \sin(\omega t)\) reaches the maximal magnitude.

The second column of Fig. 1 shows the second-order oscillations, i.e., the oscillations with frequency \( \omega \) of the electronic state in response to the driving field. The second-order oscillations of the electronic state of the laser-driven crystal are shown, comprising the oscil-
lutions of the electron current density as $-j_2(r) \sin(2\omega t)$ and the oscillations of the electron density as $\varphi_2 \cos(2\omega t)$. The second-order macroscopic polarizability tensor of the MgO crystal is zero because of inversion symmetry. Surprising, we find that the second-order microscopic optical response is nonzero. In order to understand this phenomenon, let us look into the second-order electronic state at $\omega_2 t = 0$ shown in Fig. 1(e). At this phase,
the second-order electron current density is zero and the magnitude of the second-order electron density is maximal.

As discussed in Sec. IIC, an even-order electron density amplitude of a centrosymmetric crystal is also centrosymmetric. Consistently, the second-order electron density in Fig. 1(e) is centrosymmetric with respect to the Mg atom. Therefore, the charge distribution in Fig. 1(e) results in zero macroscopic polarization. Analogously, the general statement that an even-order electron density amplitude of a centrosymmetric crystal is also centrosymmetric is consistent with the selection rule that the even-order macroscopic polarization of such a crystal is zero.

Figure 1(f) shows the second-order electronic state at $\omega t = \pi/4$, when the magnitude of the second-order electronic current density is at a maximum. Consistently with the discussion in Sec. IIC, the microscopic second-order electron current density is antisymmetric with respect to the center of symmetry.

The third column of Fig. 1 shows the third-order oscillations of the electronic state of laser-driven MgO crystal, comprising the oscillations of the electron density as $-\varrho_3 \sin(3\omega t)$ and of the electron current density as $-j_3 \cos(3\omega t)$. Figure 1(i) shows the third-order electronic state at $\omega t = 0$, which is given by the third-order electron current density. Like the first-order electron current density in Fig. 1(a), $j_3(r)$ points predominantly in the direction of the driving-field polarization. Figure 1(j) shows the third-order electron density at $\omega t = \pi/6$. Interestingly, it has a very similar structure to the first-order electron density in Fig. 1(b). The charge distribution in Fig. 1(j) also clearly indicates that the third-order macroscopic polarization points along the driving-field polarization direction.

The fourth column of Fig. 1 shows the fourth-order oscillations of the electronic state that comprise the oscillations of the electron density as $\varrho_4 \cos(4\omega t)$ and of the electron current density as $-j_4 \sin(4\omega t)$. The fourth-order electron density at $\omega t = 0$ shown in Fig. 1(m) has a very similar structure to the second-order electron density in Fig. 1(e). Since the fourth-order charge distribution is centrosymmetric, it leads to zero fourth-order macroscopic polarization.

C. Crystal without inversion symmetry: GaAs

![Fig. 2: The first- and second-order microscopic optical response of a GaAs crystal at different phases of the driving electromagnetic field polarized along the (1, 1, 1) direction. A cut of a unit cell of GaAs centered at the As atom is shown. The first column shows the oscillations of the electron density and the electron current density with frequency $\omega$, second column corresponds to the frequency $\omega_2 = 2\omega$. The yellow and blue colors represent negative and positive charges, respectively.]

We now consider the microscopic optical response of a crystal without inversion symmetry, GaAs. Since GaAs
has a band gap of 1.42 eV [77], we consider optical excitation by an optical field of 1 eV photon energy, which is lower than the one used for laser-driven MgO. The off-diagonal matrix elements of the Floquet Hamiltonian scale as $\sqrt{\epsilon_{\text{exc}}/\omega}$ [54], and we have chosen a driving-field intensity of $4 \times 10^{11}$ W/cm$^2$ to keep this factor the same as in the calculation of laser-driven MgO. 28 $\times$ 28 $\times$ 28 Monkhorst-Pack grid, 4 valence and 56 conduction bands, and 151 blocks of the Floquet-Bloch Hamiltonian are necessary to converge the results. We correct the band gap with a scissors shift of 0.42 eV.

The first and second columns of Fig. 2 show, respectively, the first- and second-order oscillations of the electronic state of GaAs driven by an optical field polarized along the $(1,1,1)$ direction. The first-order oscillations of laser-driven GaAs comprise the oscillations of the electron current density as $-j_1(r) \cos(\omega t)$ and the oscillations of the electron density as $-\rho_1 \sin(\omega t)$ as in the case of MgO.

Figure 2(a) shows the first-order electron current density at $\omega t = 0$. The vector field $-j_1(r)$ clearly points along the driving-field polarization direction in agreement with the selection rule that the macroscopic first-order polarization of GaAs is aligned with the electric field [69]. Figure 2(b) shows the first-order electron density at $\omega t = 0$. This charge distribution has a much more complex structure than that of the first-order charge distribution of MgO in Fig. 1(a). It does not have inversion symmetry, but has a three-fold rotational symmetry with respect to the driving-field polarization direction $(1,1,1)$. The positive charge alternates with the negative charge along the $(1,1,1)$ direction.

The second column of Fig. 2 shows the second-order oscillations of the electronic state that comprise the oscillations of the electron density as $\rho_2 \cos(2\omega t)$ and of the electron current density as $-j_2 \sin(2\omega t)$. According to the second-order susceptibility tensor of the space group F\overline{4}3m [69], the second-order macroscopic polarization of GaAs driven by an electric field polarized along the $(1,1,1)$ direction is also aligned along $(1,1,1)$. Figure 2(c) shows the second-order electron density at $\omega t = 0$. It also displays a three-fold rotational symmetry with respect to the driving-field polarization direction $(1,1,1)$. The positive charge alternates with the negative charge along the $(1,1,1)$ direction in agreement with the macroscopic polarization aligned along $(1,1,1)$.

The magnitude of the second-order electron current density reaches the maximum at $\omega t = \pi/4$ and is shown in Fig. 2(f). It has a very complex structure that is difficult to characterize. We calculate the volume integral of $-j_2$ and find that it indeed points in the $(1,1,1)$ direction in agreement with the selection rule for the second-order macroscopic polarization.

The first and second columns of Fig. 3 show, respectively, the first- and second-order oscillations of the electronic state of GaAs driven by a field polarized along the $(1,0,0)$ direction. Figure 3(a) shows the first-order electron current density at $\omega t = 0$, when its magnitude is at a maximum. The vector field clearly points along the driving-field polarization direction $(1,0,0)$. This is in agreement with the alignment of the first-order macroscopic polarization of GaAs with the electric field [69].

Figure 3(b) shows the first-order electron density at $\omega t = \pi/2$. It has an even more complex structure than that of the first-order electron density of GaAs driven by an optical field polarized along the $(1,1,1)$ direction in Fig. 2(b). It has two-fold rotational symmetry with respect to the direction of the driving-field polarization $(1,0,0)$. It is not obvious how the charge distribution in

![Fig. 3: Same as for Fig. 2, except the driving field is polarized along the $(1,0,0)$ direction.](image-url)
Fig. 3(b) results in the first-order macroscopic polarization along (1, 0, 0). One may notice that negative charges alter with positive charges in the x direction, when looking at charges around the bottom Ga atoms.

According to the second-order susceptibility tensor of GaAs [69], its second-order macroscopic polarization is zero for a driving field polarized along the x direction. As in the case of MgO, we obtain that the second-order microscopic optical response is indeed nonzero. Figure 3(e) shows the second-order electron density at \( \omega t = 0 \). It also has two-fold rotational symmetry about the x axis. In contrast to the case of MgO, the charge distribution does not have inversion symmetry and it is not obvious that the corresponding macroscopic polarization becomes zero. Figure 3(f) shows the second-order electron current density at \( \omega t = \pi/4 \). Despite its complex structure, we find in our calculations that its volume integral is indeed zero in agreement with the zero second-order macroscopic density amplitudes:

\[
E_x(\omega_{ks}, -\omega_{in} - \mu \omega) = \frac{1}{2 \pi} \int_{-\pi}^{\pi} E_x(\omega_{ks}, -\omega_{in} - \mu \omega) e^{i \omega t} dt.
\]

where \( \omega_{ks} \) is the energy of a scattered photon with momentum \( s \), the sum over \( s \) refers to the sum over polarization vectors of the scattered photons \( \epsilon^*_{x,s,ks} \) and \( \omega_{in} \) is the mean photon energy of the incoming x-ray beam. The quasielastic contribution is due to x-ray scattering caused by transitions only within the manifold of initially occupied laser-dressed states. The inelastic contribution is due to x-ray scattering with final states that are different from initially occupied laser-dressed states. The quasielastic part is present only at scattering vectors coinciding with the reciprocal lattice vectors \( G \). The inelastic contribution is present at all scattering vectors.

The quasielastic contribution is due to x-ray scattering caused by transitions only within the manifold of initially occupied laser-dressed states. The inelastic contribution is due to x-ray scattering with final states that are different from initially occupied laser-dressed states. Since we use the dipole approximation for the interaction of the optical field and the crystal, the quasielastic part is present only at scattering vectors coinciding with the reciprocal lattice vectors \( G \). The inelastic contribution is present at all scattering vectors.

\[
P_{\text{q.e.}}(G) = \sum_{\mu} \int d^3 r e^{i G \cdot r} \tau_0 \rho_\mu(r).
\]

Here, \( \rho_\mu(r) \) is related to the Fourier transform of the \( \mu \)-th order density amplitudes:

\[
P_{\text{q.e.}}(\omega_{ks}, G) = P_0 \sum_{\mu} \tilde{E}_x(\omega_{ks}, -\omega_{in} - \mu \omega)
\times \int d^3 r e^{i G \cdot r} \rho_\mu(r)^2.
\]

where \( \tilde{E}_x(\omega_{ks}, -\omega_{in} - \mu \omega) = \frac{1}{\sqrt{2 \pi}} e^{-\frac{(\omega_{ks} - \omega_{in} - \mu \omega)^2}{2 \ln 2}}/8 \ln 2 \)

are Gaussian-shaped functions centered at scattered energies \( \omega_{in} + \mu \omega \).

Expanding the modulus squared in Eq. (43), we obtain an expression for the quasielastic scattering probability \( P_{\text{q.e.}}(G) \) as a function of scattered energy and the time of the probe-pulse arrival.
\[ P_{\text{q.e.}}(\mathbf{G}) = P_0 \sum_\mu \tilde{E}_\mu^2 \left[ \int d^3 r e^{i \mathbf{G} \cdot \mathbf{r}} \tilde{\rho}_\mu(\mathbf{r}) \right]^2 \]

\[ + 2P_0 \sum_{\mu, \Delta \mu > 0} \tilde{E}_{\mu+\Delta \mu} \tilde{E}_{\mu} \left\{ \cos(\Delta \mu \omega t_p) \Re \left[ \int d^3 r e^{i \mathbf{G} \cdot \mathbf{r}} \tilde{\rho}_{\mu+\Delta \mu}(\mathbf{r}) \int d^3 r e^{-i \mathbf{G} \cdot \mathbf{r}} \tilde{\rho}_{\mu}(\mathbf{r}) \right] \right. \]

\[ - \sin(\Delta \mu \omega t_p) \Im \left\{ \int d^3 r e^{i \mathbf{G} \cdot \mathbf{r}} \tilde{\rho}_{\mu+\Delta \mu}(\mathbf{r}) \int d^3 r e^{-i \mathbf{G} \cdot \mathbf{r}} \tilde{\rho}_{\mu}(\mathbf{r}) \right\} \]  

The first sum over \( \mu \) in the expression above is time-independent. It is given by Gaussian-shaped functions centered at scattered energies \( \omega_s + \mu \omega \) and describes \( \mu \)-th order side peaks to the main Bragg peak of a crystal. Their amplitudes are time-independent and are given by the Fourier transforms of the density amplitudes. This term contribute to the quasielastic scattering probability in both subcycle-resolved and subcycle-unresolved measurements.

The second sum in Eq. (46) is time-dependent and contributes only in a subcycle-resolved measurement. The time-dependent terms in the sum over \( \mu \) and \( \Delta \mu \) are due to the interference between the side peaks of \( \mu \)-th and \( (\mu + \Delta \mu) \)-th order. They are proportional to the product of two Gaussian-shaped functions, which is itself a Gaussian-shaped function

\[ \tilde{E}_{\mu+\Delta \mu} \tilde{E}_\mu = e^{-(\Delta \mu \omega \tau_p)^2/16 \ln 2} \tilde{E}_{(\mu+\Delta \mu)/2}^2 \]  

centered at \( \omega_s + (\mu + \Delta \mu) \omega/2 \). These terms are nonzero as long as the Gaussian functions \( \tilde{E}_{\mu+\Delta \mu} \) and \( \tilde{E}_\mu \) spectrally overlap. We use the criterion that if the factor \( e^{-(\Delta \mu \omega \tau_p)^2/16 \ln 2} \) is greater than 0.01, the corresponding interference terms cannot be neglected. Then, if the probe-pulse duration \( \tau_p \) is less than 1.14 \( T/\Delta \mu \), where \( T = 2\pi/\omega \) is the period of the optical-field cycle, the temporal resolution is sufficient to resolve the oscillations with the frequency \( \Delta \mu \omega \).

For example, if the optical field has a photon energy of 1.55 eV, then the optical period \( T \) is 2.67 fs. An x-ray probe pulse with a duration shorter than 3 fs would provide a temporal resolution that is sufficient to resolve oscillations with the frequency \( \omega \). The time-dependent part of the spectrum in the spectral interval between \( \omega_{in} \) and \( \omega_{in} + \omega \) is then given by the interference terms between the main peak and the first-order side peak and equals

\[ 2T_0 \tilde{E}_0 \cos(\omega t_p) \Re \left[ \int d^3 r e^{i \mathbf{G} \cdot \mathbf{r}} \tilde{\rho}_1(\mathbf{r}) \int d^3 r e^{-i \mathbf{G} \cdot \mathbf{r}} \tilde{\rho}_0(\mathbf{r}) \right] \]

\[ - 2T_0 \tilde{E}_0 \sin(\omega t_p) \Im \left[ \int d^3 r e^{i \mathbf{G} \cdot \mathbf{r}} \tilde{\rho}_1(\mathbf{r}) \int d^3 r e^{-i \mathbf{G} \cdot \mathbf{r}} \tilde{\rho}_0(\mathbf{r}) \right] \]

The time-dependent part of the spectrum in the spectral interval between \( \omega_{in} + \omega \) and \( \omega_{in} + 2\omega \) is given by the interference terms between the first- and second-order side peaks and equals to

\[ 2T_0 \tilde{E}_1 \cos(\omega t_p) \Re \left[ \int d^3 r e^{i \mathbf{G} \cdot \mathbf{r}} \tilde{\rho}_2(\mathbf{r}) \int d^3 r e^{-i \mathbf{G} \cdot \mathbf{r}} \tilde{\rho}_1(\mathbf{r}) \right] \]

\[ - 2T_0 \tilde{E}_1 \sin(\omega t_p) \Im \left[ \int d^3 r e^{i \mathbf{G} \cdot \mathbf{r}} \tilde{\rho}_2(\mathbf{r}) \int d^3 r e^{-i \mathbf{G} \cdot \mathbf{r}} \tilde{\rho}_1(\mathbf{r}) \right] \]

A. Symmetry of the Fourier transform of the electron density amplitudes

In order to analyze the interference terms in more detail, let us look into the Fourier transform of the density amplitudes. As we have shown in Sec. IIB1, the even-order density amplitudes of the laser-driven crystal \( \tilde{\rho}_{\text{even}}(\mathbf{r}, t) = \tilde{\rho}_{\text{even}}(\mathbf{r})/2 \) are real functions and the odd-order density amplitudes \( \tilde{\rho}_{\text{odd}}(\mathbf{r}, t) = i \tilde{\rho}_{\text{odd}}(\mathbf{r})/2 \) are purely imaginary. Thus, we can represent the Fourier transform of an even-order density amplitude as

\[ \int d^3 r e^{i \mathbf{G} \cdot \mathbf{r}} \tilde{\rho}_{\text{even}}(\mathbf{r}) = \frac{1}{2} P_{\text{even}}^g (\mathbf{G}) + \frac{i}{2} P_{\text{even}}^s (\mathbf{G}) \]

and the Fourier transform of an odd-order density amplitude as

\[ \int d^3 r e^{i \mathbf{G} \cdot \mathbf{r}} \tilde{\rho}_{\text{odd}}(\mathbf{r}) = \frac{i}{2} P_{\text{odd}}^g (\mathbf{G}) - \frac{1}{2} P_{\text{odd}}^s (\mathbf{G}) \]

where the functions

\[ P_{\mu}^g (\mathbf{G}) = \int d^3 r \cos(\mathbf{G} \cdot \mathbf{r}) \tilde{\varrho}_\mu(\mathbf{r}) \]

and

\[ P_{\mu}^s (\mathbf{G}) = \int d^3 r \sin(\mathbf{G} \cdot \mathbf{r}) \tilde{\varrho}_\mu(\mathbf{r}) \]

are real. The function \( P_{\mu}^g (\mathbf{G}) \) is an even function of \( \mathbf{G} \)

\[ P_{\mu}^g (\mathbf{G}) = P_{\mu}^g (-\mathbf{G}) \]

whereas \( P_{\mu}^s (\mathbf{G}) \) is an odd function of \( \mathbf{G} \)

\[ P_{\mu}^s (\mathbf{G}) = -P_{\mu}^s (-\mathbf{G}) \]

In Eqs. (52) and (53), we return to the real-valued representation of the density amplitudes, \( \tilde{\varrho}_\mu \).
1. Crystals with an inversion symmetry

We now consider the Fourier transform of density amplitudes of crystals with spatial inversion symmetry. We have shown in Sec. IIC that such even-order density amplitudes \( \tilde{\rho}_{\mu_{\text{even}}}(r) \) are symmetric with respect to the transformation \( r \rightarrow -r \). As a result, the integral \( \mathcal{P}_{\mu_{\text{even}}}(G) \) is zero for the even-order amplitudes of a crystal with inversion symmetry. Hence, the Fourier transform of \( \tilde{\rho}_{\mu_{\text{even}}}(r) \) is a real function

\[
\int d^3r e^{iG \cdot r} \tilde{\rho}_{\mu_{\text{even}}}(r) = \frac{1}{2} \mathcal{P}_\mu(G). \tag{56}
\]

The odd-order density amplitudes of a crystal with inversion symmetry \( \tilde{\rho}_{\mu_{\text{odd}}}(r) \) are antisymmetric with respect to the transformation \( r \rightarrow -r \). Thus, the integrals \( \mathcal{P}_{\mu_{\text{odd}}}(G) \) are zero, so that the Fourier transform of an odd-order density amplitude of a crystal with inversion symmetry is also a real function

\[
\int d^3r e^{iG \cdot r} \tilde{\rho}_{\mu_{\text{odd}}}(r) = -\frac{1}{2} \mathcal{P}_\mu(G). \tag{57}
\]

Thus, we obtain that the imaginary parts of the products \( \int d^3r e^{iG \cdot r} \tilde{\rho}_{\mu_{\text{odd}}} \tilde{\rho}_{\mu_{\text{even}}} \) entering the relation for the quasielastic probability in Eq. (46) are zero. As the consequence, the time evolution of the quasielastic scattering involves only \( \cos(\Delta \mu \omega t_p) \) functions:

\[
P_{\text{q.e.}}(G, \omega) = P_0 \sum_\mu \tilde{\epsilon}_\mu^2 \left| \int d^3r e^{iG \cdot r} \tilde{\rho}_\mu(r) \right|^2 + 2P_0 \sum_{\mu, \Delta \mu > 0} \tilde{\epsilon}_\mu + \Delta \mu \tilde{\epsilon}_\mu \cos(\Delta \mu \omega t_p) \operatorname{Re} \left[ \int d^3r e^{iG \cdot r} \tilde{\rho}_{\mu + \Delta \mu}(r) \int d^3r e^{-iG \cdot r} \tilde{\rho}_\mu^*(r) \right]. \tag{58}
\]

The time-dependent terms that evolve as \( \cos(\Delta \mu_{\text{odd}} \omega t_p) \) are antisymmetric functions of \( G \). The terms that evolve as \( \cos(\Delta \mu_{\text{even}} \omega t_p) \) are centrosymmetric functions of \( G \).

B. Time dependence of the x-ray-optical wave mixing signal

1. Crystal with inversion symmetry

We first study the ultrafast x-ray scattering signal from the laser-driven MgO crystal, which is a crystal with inversion symmetry. We consider the same parameters of the optical driving field as in Sec. IIIB, namely, an intensity of \( 2 \times 10^{12} \) W/cm\(^2\) and polarization along \((0, 0, 1)\). The optical field has a photon energy of \( \omega = 1.55 \) eV, which corresponds to an optical period of \( T = 2\pi/\omega = 2.67 \) fs. We assume the duration of the probe nonresonant x-ray pulse is 2.0 fs, which is sufficient to resolve first-order oscillations of the electronic state of laser-driven MgO. Figure 4 shows the energy-resolved quasielastic and inelastic scattering signals at the scattering vectors \( G = (0, 0, 2) \) and \( G = (0, 0, -2) \) at different probe-pulse arrival times. Scattering signals are normalized to the main Bragg peak at \( G = (0, 0, 2) \), which is centered at the scattered energy \( \omega_s = \omega_{\text{in}} \).

First, we observe that inelastic scattering from MgO is considerable only at \( \omega_s < \omega_{\text{in}} \), which has the following reason. Inelastic scattering from a field-free MgO crystal would appear only at scattered energies less than the incoming x-ray photon energy minus the band-gap of 7.8 eV. When MgO is driven by the optical field, the inelastic signal is modulated. The inelastic scattering is then nonzero at higher scattered energies, but decays fast with the increasing scattered energy. Thus, we will analyze the probability of quasielastic scattering at \( \omega_s > \omega_{\text{in}} \), where it dominates in the total x-ray scattering probability from a laser-driven band-gap crystal.

Second, we find that the quasielastic scattering signal at \( t_p = 0 \) [Figs. 4(a) and (b)] and at \( t_p = T/2 \) [Figs. 4(e) and (f)] is non-centrosymmetric with respect to \( G \). In order to understand the origin of the nonsymmetry of the signal, we apply Eqs. (56) and (57) to Eq. (58):

\[
P_{\text{q.e.}}(G, \omega_s > \omega_{\text{in}}) = \frac{P_0}{4} \left\{ \tilde{\epsilon}_0^2 \left| \mathcal{P}_0^s(G) \right|^2 - 2\tilde{\epsilon}_1 \tilde{\epsilon}_0 \cos(\omega t_p) \mathcal{P}_1^s(G) \mathcal{P}_0^s(G) + \tilde{\epsilon}_2^2 \left| \mathcal{P}_1^s(G) \right|^2 \right. \nonumber
\]

\[
- \left. 2\tilde{\epsilon}_2 \tilde{\epsilon}_1 \cos(\omega t_p) \mathcal{P}_2^s(G) \mathcal{P}_1^s(G) + \tilde{\epsilon}_2^2 \left| \mathcal{P}_2^s(G) \right|^2 - 2\tilde{\epsilon}_3 \tilde{\epsilon}_2 \cos(\omega t_p) \mathcal{P}_3^s(G) \mathcal{P}_1^s(G) + \cdots \right\}. \tag{59}
\]

Here, we took into account that only nearest-neighbor side peaks can interfere for the chosen probe-pulse dura-
In the following, we demonstrate that a nonzero microscopic electron current is the origin of the non-symmetry term. The terms in the above expression are ordered according to their position in the spectrum. The quasielastic scattering signal consists of time-independent and time-dependent contributions. The time-independent contribution is due to the main Bragg peak centered at the scattered energy $\omega_s = \omega_{in}$ and its side peaks centered at scattered energies $\omega_{in} + \mu \omega$. The corresponding terms are centrosymmetric with respect to the transformation $\mathbf{G} \rightarrow -\mathbf{G}$. The relative intensities of the side peaks are shown with gray lines in Fig. 4. They are proportional to the absolute values of the Fourier transforms of the corresponding $\mu$th-order optically induced charge distributions. We calculated the intensities of side peaks of the laser-driven MgO crystal in Ref. 38 and explained that the sum-frequency signal, which was experimentally observed in x-ray diffraction from laser-driven diamond in Ref. [34], is the first-order side peak in our terminology.

The time-dependent contribution is due to the interference terms between the nearest-neighbor side peaks of the $\mu$th and $(\mu + 1)$th order that are given by Gaussian-shaped functions centered at scattered energies $\omega_{in} + (\mu + 1/2)\omega$. The interference terms are antisymmetric with respect to the transformation $\mathbf{G} \rightarrow -\mathbf{G}$.

In the following, we demonstrate that a nonzero microscopic electron current is the origin of the non-symmetry

![Figure 4](image-url)  
**Fig. 4:** Intensities of quasielastic and inelastic x-ray scattering signals at $\mathbf{G} = (0, 0, 2)$ and $\mathbf{G} = (0, 0, -2)$ from the laser-dressed MgO crystal at different probe-pulse arrival times as a function of $\omega_s - \omega_{in}$. The intensities are normalized to the intensity of the main Bragg peak of MgO at $\mathbf{G} = (0, 0, 2)$. The gray vertical lines are situated at the positions of the side peaks, $\omega_s - \omega_{in} = \mu \omega$, and their heights correspond to their relative intensities.

![Figure 5](image-url)  
**Fig. 5:** Difference of the relative intensities of quasielastic scattering at $\mathbf{G} = (0, 0, 2)$ and $\mathbf{G} = (0, 0, -2)$ from the laser-dressed MgO crystal at different probe-pulse arrival times as a function of $\omega_s - \omega_{in}$ (a) in the range $[0: \omega]$ and (b) in the range $[\omega: 2\omega]$. 


of the quasielastic scattering. We apply the relation
\[ \operatorname{div} j_\mu(r) = -i\omega \frac{d}{dt} G \cdot \int d^3 r e^{iG \cdot r} j_\mu(r). \]  
(60)

This relation follows from a general relation for a Fourier transform of a divergence of a vector field. The interference between the main Bragg peak and the first-order side peak [the second term in Eq. (59)] is then proportional to
\[ \mathcal{P}^q_0(G) \left[ G \cdot \int d^3 r e^{iG \cdot r} j_1(r) \right] \cos(\omega t_p). \]  
(61)

Hence, the time evolution of the interference term coincides with the time evolution of the first-order oscillations of the electron current density \(-j_1(r)\co \omega t_p\) [cf. Fig. 1(a)-(d)]. As long as the projection of the first-order electron current density on a direction parallel to \(G\) is nonzero, the interference term is antisymmetric with respect to \(G\).

The interference term between the first- and the second-order side peaks [the fourth term in Eq. (59)] is proportional to
\[ \left[ G \cdot \int d^3 r e^{iG \cdot r} j_1(r) \right] \left[ G \cdot \int d^3 r e^{iG \cdot r} j_2(r) \right] \cos(\omega t_p). \]  
(62)

The second-order electron current density does not have any distinguished direction [cf. Fig. 1(e)-(h)] and the second term is a centrosymmetric function of \(G\) and \(-G\). Thus, the interference term is antisymmetric again due to the first-order electron current density. Its temporal dependence also follows the oscillations of the first-order electron current density.

The interference term between the second- and third-order side peaks [the sixth term in Eq. (59)] is proportional to
\[ \left[ G \cdot \int d^3 r e^{iG \cdot r} j_2(r) \right] \left[ G \cdot \int d^3 r e^{iG \cdot r} j_3(r) \right] \cos(\omega t_p). \]  
(63)

and it is antisymmetric due to the third-order electron current density [cf. Fig. 1(i)-(l)]. The third-order electron current density oscillates as \(\cos(3\omega t_p)\), which is faster than the \(\cos(\omega t_p)\) oscillations of the antisymmetric term. The discrepancy between the temporal dependence is consistent with the statement that the x-ray-probe pulse of the chosen duration does not provide a sufficient temporal resolution to resolve oscillations with the frequency \(3\omega\).

At \(t_p = 0\), the direction of the first-order electron current density is parallel to \(G = (0,0,2)\), and the corresponding quasielastic signal in Figs. 4(a) and (b) is non-centrosymmetric. At \(t_p = T/4\) and \(t_p = 3T/4\), the first-order electron current density is zero, and the corresponding signals in Figs. 4(c), (d), (g) and (h) are centrosymmetric. At \(t_p = T/2\), the direction of the first-order electron current density is opposite to that at \(t_p = 0\). The quasielastic signals at \(G = (0,0,2)\) and \(G = (0,0,-2)\) switch between each other relatively to those at \(t_p = 0\) [cf. Figs. 4(e) and (f)]. The quasielastic signals are also symmetric (antisymmetric) functions of \(\omega t_p\) when they are symmetric (antisymmetric) with respect to \(G\).

The time-dependent part of the signal can be easily disentangled from the total signal. It is simply the difference between quasielastic scattering signal at opposite \(G\), \(P_{q.e.}(G) - P_{q.e.}(-G)\). Figure 5(a) shows \(P_{q.e.}(G) - P_{q.e.}(-G)\) for \(G = (0,0,2)\) in the range of scattered energies \(\omega s \in [\omega in, \omega in + \omega]\) at different probe-pulse arrival times. As discussed above, this difference is given by the interference term between the main Bragg peak and the first-order side peak, which is a Gaussian-shaped function centered at \(\omega in + \omega/2\) with an amplitude proportional to \(-4P_{q.e.}^3(G)P_{q.e.}^2(G)\cos(\omega t_p)\).

\(P_{q.e.}^0(G)\) is approximately the Fourier transform of the unperturbed density of MgO. Since \(P_{q.e.}^0(G) > 0\) and the interference term at \(t_p = 0\) is positive, \(P_{q.e.}^1(G)\) is negative. Its amplitude can be reconstructed by measuring the intensity of the first-order side peak in a subcycle-unresolved measurement, which is proportional to \(|P_{q.e.}^1(G)|^2\). Alternatively, one can determine \(|P_{q.e.}^1(G)|\) by dividing the maximum intensity of the interference term by \(4P_{q.e.}^0(G)e^{-(\omega s)^2/16}\ln2\) [cf. Eq. (47)]. Thus, we obtain that \(P_{q.e.}^1(G)/P_{q.e.}^3(G) = -1.7 \times 10^{-3}\) for \(G = (0,0,2)\).

We determined \(P_{q.e.}^1(G)\) and can reconstruct \(P_{q.e.}^2(G)\) from the difference \(P_{q.e.}(G) - P_{q.e.}(-G)\) for \(G = (0,0,2)\) in the range of scattered energies \(\omega s \in [\omega in, \omega in + 2\omega]\) shown in Fig. 5(b). The difference is given by the interference term between the first- and the second-order side peaks. It should be a Gaussian-shaped function centered at \(\omega in + 3\omega/2\), but its shape is affected by the Gaussian function centered at \(\omega in + \omega/2\). The amplitude of the peak is still proportional to \(-4P_{q.e.}^2(G)P_{q.e.}^3(G)\cos(\omega t_p)\), and we obtain that \(P_{q.e.}^2(G)/P_{q.e.}^3(G) = -2.0 \times 10^{-3}\) at \(G = (2,0,0)\) using the same algorithm. Such a procedure to determine the Fourier transform of the density amplitudes can be repeated as long as the interference terms are detectable. The density amplitudes in real space can be reconstructed if the scattering signal at various \(G\) is measured.

It may be surprising that \(|P_{q.e.}^2(G)| > |P_{q.e.}^1(G)|\) at \(G = (0,0,2)\) in Fig. 4, although the maximum amplitude of the first-order electron current density is higher than that of the second-order electron current density (cf. Fig. 1). As we discussed, \(P_{q.e.}^\mu(G)\) is proportional to \(G \cdot \int d^3 r e^{iG \cdot r} j_\mu(r)\) [cf. Eq. (60)]. The first-order electron current density of MgO is localized around oxygen atoms. This means that its Fourier transform should be a delocalized function of \(G\). Thus, \(P_{q.e.}^1(G)\) should remain considerable at increasing \(G\) parallel to \((0,0,1)\). The second-order electron current density is less localized.
The first unexpected result was that the intensities of even-order side peaks [cf. the gray lines in Fig. 4] were strongly reduced.

As mentioned above, when calculating the time-independent side peaks to the main Bragg peak of laser-driven MgO in Ref. 38, we found several phenomena that we could not explain. We can now understand the behavior of the side peaks using results of Sec. II and Fig. 1. The first unexpected result was that the intensities of even-order side peaks [cf. the gray lines in Fig. 4] were nonzero, although even-order harmonics of MgO are zero. As we found in Sec. III, the microscopic even-order optical response of MgO is nonzero although it results in zero macroscopic optical response. In the optical-x-ray wave mixing experiment, x rays give access to the atomic scale and reveal the microscopic optical response.

The second surprising observation was that the intensities of the odd-order side peaks were zero at \( \mathbf{G} \) perpendicular to the driving-field polarization \( \epsilon \), whereas the intensities of the even-order side peaks did not change considerably at \( \mathbf{G} \perp \epsilon \). Comparing the odd-order and even-order amplitudes of the electron density, and the odd-order and even-order amplitudes of the electron current density in Fig. 1, this behavior becomes clear. The odd-order electron current densities are aligned along the driving-field polarization direction, such that \( \mathbf{G} \cdot \int d^3\mathbf{r} e^{i\mathbf{G}\cdot\mathbf{r}} j'_{p}(\mathbf{r}) \) is zero at \( \mathbf{G} \perp \epsilon \). The even-order density amplitudes are close to a spherically symmetric distribution and their Fourier components do not have such a pronounced angular dependence. That is why their Fourier components do not strongly depend on an angle between \( \mathbf{G} \) and \( \epsilon \).
2. Crystal with broken inversion symmetry

We now describe the subcycle-resolved x-ray scattering signal from laser-dressed GaAs, which is a crystal without inversion symmetry. We use the same parameters of the optical field as in Fig. 3 in Sec. III C, namely, an intensity of $4 \times 10^{11}$ W/cm$^2$, a photon energy of $\omega = 1$ eV and polarization along $(1,0,0)$. The optical period of the driving field is 4.14 fs. We assume a probe x-ray pulse duration of 3.5 fs, which provides sufficient temporal resolution to resolve the oscillations of the electronic state of laser-dressed GaAs with frequency $\omega$.

Figure 7 shows the energy-resolved quasielastic and inelastic scattering signals at the scattering vectors $G = (1,1,1)$ and $G = (-1,-1,-1)$ at different probe-pulse arrival times. Scattering signals are normalized to the main Bragg peak at $G = (1,1,1)$, which is centered at the scattered energy $\omega_s = \omega_{in}$. The inelastic contribution is much higher than the inelastic contribution to the scattering signal from laser-driven MgO in Fig. 4. This is due to the smaller band gap of GaAs, which means that the inelastic signal from a field-free crystal is energetically closer to the main Bragg peak. The inelastic contribution is still much smaller than the intensities of the side peaks at $\omega_s > \omega_{in}$. The gray lines in Fig. 7 show the intensities of the side peaks relative to the main Bragg peak. We again observe that the intensity of the second-order side peak is nonzero despite zero second-order macroscopic optical response of GaAs, when the driving field is polarized along $(1,0,0)$.

We have chosen to analyze the signal at the scattering vectors $G = \pm(1,1,1)$, because the Fourier transform of the field-free electron density of the GaAs crystal at $G = \pm(1,1,1)$ is complex and both its centrosymmetric part $P^0_\mu(G)$ and antisymmetric part $P^a_\mu(G)$ are nonzero. When we considered a crystal with inversion symmetry, one of the functions $P^0_\mu(G)$ and $P^a_\mu(G)$ was zero, depending on the parity of $\mu$. Now, both $P^0_\mu(G)$ and $P^a_\mu(G)$ can be nonzero for a crystal with broken inversion symmetry. Let us now see how this affects the quasielastic scattering probability applying the results of Sec. IV A to the expression for the quasielastic scattering probability in Eq. (46), which leads to

\[
P_{q.e.}(G, \omega_s > \omega_{in}) = \frac{P_0 \tilde{E}_0^2}{4} \left\{ (P^0_\mu(G))^2 + (P^a_\mu(G))^2 \right\} + \frac{P_0 \tilde{E}_1 \tilde{E}_0}{2} \left\{ \cos(\omega t_p) \left[ P^0_\mu(G)P^0_\mu(G) - P^a_\mu(G)P^a_\mu(G) \right] \right. \\
- \sin(\omega t_p) \left[ P^0_\mu(G)P^a_\mu(G) + P^a_\mu(G)P^0_\mu(G) \right] \left. \right\} + \frac{P_0 \tilde{E}_2 \tilde{E}_1}{2} \left\{ - \cos(\omega t_p) \left[ P^0_\mu(G)P^0_\mu(G) - P^a_\mu(G)P^a_\mu(G) \right] \right. \\
+ \sin(\omega t_p) \left[ P^0_\mu(G)P^a_\mu(G) + P^a_\mu(G)P^0_\mu(G) \right] \left. \right\} + \frac{P_0 \tilde{E}_2 \tilde{E}_2}{2} \left\{ (P^0_\mu(G))^2 + (P^a_\mu(G))^2 \right\} + \cdots
\]

The terms in this expression are ordered according to their position in the spectrum. The time-dependent part of the quasielastic scattering probability consists now of two parts. The first part evolves in time as $\cos(\omega t_p)$ and coincides with the time dependence of the first-order oscillation of the electron current density $-j_1(r) \cos(\omega t)$. Similar to the time-dependent part of a crystal with inversion symmetry, it is an antisymmetric function of $G$ and can be disentangled from the signal by taking the difference at opposite $G$. The difference of the signals at opposite $G$ is shown in Fig. 8(a) in the spectral range where the main peak and the first-order side peak interfere. The second contribution, which is absent for a crystal with inversion symmetry, evolves in time as $\sin(\omega t_p)$ and coincides with the time evolution of the first-order oscillation of the electron density $-g_1(r) \sin(\omega t_p)$. It is a centrosymmetric function of $G$. Since the time-independent contribution to the quasielastic scattering is also centrosymmetric, it is less trivial to disentangle the second contribution. One should first subtract the time-independent part $P_{t.-ind.}$ from the signal, which can be obtained by taking the sum of signals at opposite $G$ at the probe-pulse arrival time $t_p = 0$: $2P_{t.-ind.} = P_{q.e.}(G, t_p = 0) + P_{q.e.}(-G, t_p = 0)$. After the time-independent part is subtracted, the sum of the remaining part of the signals at opposite $G$ gives the second contribution. This sum is shown in Fig. 8(b) in the spectral range where the main peak and first-order side peak interfere.

Let us now consider how to reconstruct the electron density amplitudes from the quasielastic scattering signal. The Fourier transform of the electron density amplitudes $\int d^3r e^{iG \cdot r} q_\mu(r)$ is complex functions that can be represented as $\left| \int d^3r e^{iG \cdot r} q_\mu(r) e^{i\omega s(G)} \right|$. It follows from the definition of $P^0_\mu(G)$ and $P^a_\mu(G)$ in Sec. IV A that

\[
P^0_\mu(G) = \left| \int d^3r e^{iG \cdot r} q_\mu(r) \right| \cos[\alpha_\mu(G)], \quad (65)
\]
\[
P^a_\mu(G) = \left| \int d^3r e^{iG \cdot r} q_\mu(r) \right| \sin[\alpha_\mu(G)]. \quad (66)
\]
Thus, we can rewrite the above expression in Eq. (64) as

\[
P_{\text{q.e.}}(\mathbf{G}, \omega_s > \omega_{in}) = \frac{P_0 e^2}{4} \left[ \left| \int d^3r e^{i\mathbf{G} \cdot \mathbf{r}} \varrho_0(r) \right|^2 + \frac{P_0 \bar{e}_1 \bar{e}_0}{2} \left| \int d^3r e^{i\mathbf{G} \cdot \mathbf{r}} \varrho_1(r) \right| \left| \int d^3r e^{i\mathbf{G} \cdot \mathbf{r}} \varrho_0(r) \right| \sin(\omega t_p - \alpha_0 + \alpha_1) \right] (67)
\]

\[
+ \frac{P_0 e^2}{4} \left| \int d^3r e^{i\mathbf{G} \cdot \mathbf{r}} \varrho_1(r) \right|^2 - \frac{P_0 \bar{e}_2 \bar{e}_1}{2} \left| \int d^3r e^{i\mathbf{G} \cdot \mathbf{r}} \varrho_1(r) \right| \left| \int d^3r e^{i\mathbf{G} \cdot \mathbf{r}} \varrho_2(r) \right| \sin(\omega t_p - \alpha_1 + \alpha_2)
\]

\[
+ \frac{P_0 e^2}{4} \left| \int d^3r e^{i\mathbf{G} \cdot \mathbf{r}} \varrho_2(r) \right|^2 + \ldots .
\]

The scattering signal evolves in time out of phase with the electric field oscillation of the driving field. The phase shift is determined by the phases of the spatial Fourier transform of the \( \mu \)-th optically-induced charge distributions.

The amplitudes \( \left| \int d^3r e^{i\mathbf{G} \cdot \mathbf{r}} \varrho_\mu(r) \right| \) can be reconstructed from the intensity of the side peaks centered at scattered energies \( \omega_s = \omega_{in} + \mu \omega \). To reconstruct the phases \( \alpha_\mu(\mathbf{G}) \), it is necessary to know the phase of the Fourier transform of the zero-order density amplitude. In our calculations, we obtain \( \alpha_0(\mathbf{G}) = -0.38\pi \) at \( \mathbf{G} = (1, 1, 1) \) for GaAs. Thus, knowing \( \alpha_0(\mathbf{G}) \) and the time evolution of the scattering signal in the range of \( \omega_s - \omega_{in} \in [0, \omega] \) in Fig. 8, we obtain the phase \( \alpha_1(\mathbf{G}) = 0.1\pi \) of the Fourier transform of the first-order optically-induced charge distribution. Repeating this procedure for the subsequent interference terms and collecting data at various \( \mathbf{G} \), the optically-induced charge distributions can be retrieved.

3. Discussion

To sum up, we have considered subcycle-resolved x-ray scattering from laser-driven crystals with a temporal resolution that is sufficient to resolve oscillations at the driving frequency \( \omega \). The total scattering signal is the sum of the inelastic scattering and the quasielastic scattering signal \( P_{\text{q.e.}}(\mathbf{G}) \). The quasielastic scattering signal is the x-ray-optical wave-mixing signal and contains information about optically-induced charge distributions and microscopic electron currents. It dominates the signal at scattered energies larger than the incoming x-ray photon energy. We found that the quasielastic scattering signal is notably noncentrosymmetric with respect to the scattering vector \( \mathbf{G} \). Thus, it contains the antisymmetric part \( (P_{\text{q.e.}}(\mathbf{G}) - P_{\text{q.e.}}(-\mathbf{G}))/2 \), and the centrosymmetric part \( (P_{\text{q.e.}}(\mathbf{G}) + P_{\text{q.e.}}(-\mathbf{G}))/2 \). The temporal evolution of the antisymmetric part follows the temporal evolution of the first-order oscillations of the electron current density \(-j_1(r) \cos(\omega t) \) [cf. Eq. (25)]. It is directly connected to the Fourier transform of the electron current density if the crystal has inversion symmetry. For crystals with broken inversion symmetry, the temporal dependence of the centrosymmetric part follows the first-order electron density \(-\varrho_1(r) \sin(\omega t) \) [cf. Eq. (21)], whereas for crystals with inversion symmetry, this part is constant.

When the temporal resolution of the measurement is higher, the temporal dependence of the x-ray-optical wave mixing signal involves higher-order oscillations. The connection of oscillations of the antisymmetric and centrosymmetric part to the oscillations of the electron current density and of the electron density, respectively, also holds in this case. Analyzing Eq. (46), it can be shown that higher-order oscilla-

![Fig. 8: (a) Difference and (b) sum of time-dependent contributions to quasielastic scattering at \( \mathbf{G} = (1, 1, 1) \) and \( \mathbf{G} = (-1, -1, -1) \) from the laser-dressed GaAs crystal at different probe-pulse arrival times as a function of \( \omega_s - \omega_{in} \) in the range \( [0 : \omega] \).](image-url)
tions of the centrosymmetric part involve only periodic functions that enter the expression for the oscillations of the electron density $\rho(r,t_p)$, namely, $\sin(\mu \omega t_p)$ and $\cos(\mu \omega t_p)$. The higher-order oscillations of the antisymmetric part involve only periodic functions $\sin(\mu \omega t_p)$ and $\cos(\mu \omega t_p)$ that enter the expression for the oscillations of the electron current density $j(r,t_p)$. Other time- and momentum-resolved techniques for measuring freely evolving electron dynamics have a similar connection to the temporal evolution of electron density and electron current density [62].

The other finding of this Section is a method to reconstruct the Fourier transform of optically-induced charge distributions including its phase. We found that the x-ray-optical wave mixing signal oscillates out of phase with the electric field of the optical pulse and the phase shift depends on the spectral range and scattering vector $\mathbf{G}$. The phase shift in the spectral range $[\omega_m + \mu \omega : \omega_m + (\mu + 1)\omega]$ is the phase difference between $\mathbf{G}$ components of the Fourier transform of the $(\mu + 1)$th and $\mu$th-order charge distributions. Thus, if the Fourier transform of the unperturbed density is known, phases of $\int d^3re^{i\mathbf{G}\cdot \mathbf{r}} \varrho_\mu(\mathbf{r})$ can be reconstructed. The amplitudes of the $\mathbf{G}$ components of the Fourier transform can be reconstructed either from the time-independent part of the x-ray-optical wave mixing signal or from a subcycle-unresolved measurement.

V. CONCLUSIONS

In this study, we reconsidered nonlinear optical response of band-gap crystals by focusing on its properties on the atomic scale. Our study applies to the regime of light-matter interaction that is either perturbative and describes conventional nonlinear optics experiments, or is non-perturbative, but still not sufficiently strong to considerably affect the band structure of the crystal considered. We developed a method to measure the microscopic optical response by means of ultrafast nonresonant x-ray scattering.

We found that, on the atomic scale, optically-induced charge distributions go far beyond the concept of a dipole and have a complex spatial structure. This structure has several interesting properties determined by the symmetry of the crystal. Time-reversal symmetry determines the phase of $\mu$th-order oscillations of the optically-induced charge distribution. Even-order charge distributions evolve as harmonics in phase with the vector potential of the optical field, whereas odd-order charge distributions evolve as harmonics in phase with the electric field. Spatial inversion symmetry of the crystal leads to the spatial inversion symmetry of $\mu$th-order optically-induced charge distributions. Thereby, even-order distributions are symmetric with respect to the transformation $\mathbf{r} \rightarrow -\mathbf{r}$, and odd-order distributions are antisymmetric. As a result, odd-order optically-induced charge distributions are aligned in such a way that macroscopic polarization is induced, and even-order distributions lead to a vanishing macroscopic polarization. Thus, even when macroscopic optical response is forbidden, charges still rearrange within the unit cell of the crystal.

The microscopic optical response can be accessed by x-rays with a wave length comparable to interatomic distances. Here, we developed a method to measure laser-driven electron dynamics on the atomic scale by means of ultrafast x-ray-optical wave mixing, i.e. ultrafast x-ray scattering during the interaction of a crystal with an optical pulse. First, we have shown that charge flow manifests itself in a notable noncentrosymmetry of the subcycle-resolved x-ray-optical wave mixing signal with respect to the scattering vector and the scattered energy. $\mu$th-order temporal oscillations of the antcentrosymmetric part of the signal are in phase with the $\mu$th-order oscillations of the electron current density. In the case of a crystal with inversion symmetry, the antcentrosymmetric part of the x-ray-optical wave mixing signal at scattering vector $\mathbf{G}$ is directly connected to the $\mathbf{G}$ component of the Fourier transform of the electron current density.

We developed a procedure to reconstruct $\mu$th-order optically-induced charge distributions $\varrho_\mu(\mathbf{r})$ from the subcycle-resolved x-ray-optical wave mixing signal. To this end, we propose to study scattering signals obtained with a temporal resolution that resolves signal oscillations with the frequency $\omega$. Such a signal comprises the Bragg peaks of the crystal, their side peaks centered at scattered energies $\omega_m + \mu \omega$ and the interference terms between nearest-neighbor peaks. The amplitudes of the Fourier transform of the $3$-th-order temporal oscillations of the antcentrosymmetric part of the signal are retrieved from the phases of the temporal oscillations of the interference terms. X-ray-optical wave mixing signals reveal even those optically-induced charge distributions that do not result in a macroscopic optical response, such as the even-order microscopic optical response of crystals with inversion symmetry.

Even though we focused our considerations to simple band-gap crystals exposed to a periodic optical excitation, we found many nontrivial properties of microscopic optical response that can be revealed with x-ray scattering. This demonstrates that x-ray-optical wave mixing techniques are powerful tools for obtaining novel insights into laser-driven dynamics in periodic materials. An atomically-resolved view on light-matter interactions will provide a deeper understanding of optically-driven electron dynamics and prompt further developments of nonlinear optics towards technological applications.
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