

Hidden linear optical response reveals crystalline symmetry

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Received 10 February 2020; revised 18 March 2020; accepted 20 March 2020; posted 20 March 2020 (Doc. ID 390183); published 15 April 2020

We show that a linear quadrupole response from a crystalline material to externally applied optical fields exists and has gone unnoticed, even though its nonlinear optical cousin has been studied and explored extensively for decades. Such a linear quadrupole response reveals the symmetry of the crystal, just as its nonlinear optical counterpart has done, and can be used to investigate phase transitions non-intrusively with high spatial and temporal resolution. © 2020 Optical Society of America

<https://doi.org/10.1364/OL.390183>

Symmetry-dependent linear and nonlinear responses of all kinds in solid and liquid crystalline materials to external stimuli reveal phases of materials. Among them optical responses are unique, as (1) they can be obtained in non-contact ways; (2) they have high spatial resolutions for microscopy; and (3) they have unmatched time resolutions for dynamic studies. Not surprisingly, symmetry-dependent nonlinear optical responses have been extensively explored for phase transition studies in 2D and 3D material systems since the early days of nonlinear optics up to very recently [1–14].

An externally applied electromagnetic field causes electrons in a solid material to produce a time and spatially varying polarization $\mathbf{P}(\mathbf{r}, t)$. $\mathbf{P}(\mathbf{r}, t)$ is a function of the electric field, the magnetic field, and their gradients [3]. The leading terms in $\mathbf{P}(\mathbf{r}, t)$ are responses that depend linearly on the electromagnetic fields. Traditionally, only the response that varies linearly with the electric field has been considered, but not the gradient of the electric field and the magnetic field. Such a truncated linear response is represented by a linear dielectric tensor of first rank and produces the usual reflected and transmitted electromagnetic waves. The linear dielectric tensor depends on the symmetry of the material in a most crude way and is thus rarely used in studies of phase transition except for melting. Nonlinear optical responses make up for the remaining terms in $\mathbf{P}(\mathbf{r}, t)$, and they depend on products of no fewer than two of the electric field, the magnetic field, and their gradients. In these cases, the nonlinear polarization varies with the electric field and the magnetic field through tensors of second or higher rank. These second or higher rank tensors were recognized to be strongly symmetry dependent from the beginning [1,2]. As a

result, nonlinear optical responses including those involving gradients of the electric field have been investigated extensively and exploited in phase transition studies since the early 1980s [3–14]. For example, Shank *et al.* and Tom *et al.* studied melting of semiconductors by measuring bulk second-order electric quadrupole responses as the crystalline solid becomes an isotropic material in the phase transition [11,12]. Heinz and coworkers studied surface phase transition on Si(111) by measuring the dipole-allowed surface second-harmonic generation from two different surface reconstructions [8]. Zhu and coworkers studied “phase transition” in evaporated gold films by measuring the bulk second-harmonic generation involving the gradient of the electric field [13]. A more recent example is the second-harmonic generation study reported by Zhao and coworkers of hidden phase transition in Sr_2IrO_4 , a material normally having inversion symmetry [14]. In this study by measuring the azimuth-dependent second-order nonlinear optical response, these authors uncovered a hidden phase that breaks inversion symmetry. This transition evaded the linear x-ray and neutron diffraction measurements. These authors further demonstrated the utility of high spatial resolution of the coherent optical measurement when they needed to examine the phase transition in a single domain instead of an average in four differently oriented domains that would have washed out the evidence of the new phase. They further showed the need to use optic pulses less than 100 fs to avoid the sample heating, a crucial requirement not met by longer optical pulses.

The success of nonlinear optical responses involving third or higher rank tensors has innocently masked the fact that the linear response to the gradient of the electric field—the quadrupole response—exists and also involves a second rank tensor [3]. This linear response can be used to reveal the symmetry and thus the phase of crystalline materials beyond the usual linear dielectric tensor.

In this Letter, we explore this forgotten linear optical response both theoretically and experimentally, partly to add the missing piece in description of optical responses to the symmetry of a crystalline material. It is easy to understand why such a second rank linear response has gone unnoticed. Compared to the leading-order linear response (i.e., the electric dipole response), it is weaker by the ratio of Bohr radius a_B to the optical wavelength λ , i.e., 10^{-3} ; thus, its contributions to reflection

and transmission are “hidden” and easily ignored. Although magneto-optic responses from a solid are as weak or weaker [15–17], they can be modulated with an externally applied magnetic field and thus are detectable using modulation schemes. We recognize that the linear optical response from a monolayer or less of dielectric materials on top of a different solid material yields signals comparable to that of a bulk linear quadrupole response, and the former has been detected routinely with ellipsometry in surface and thin film studies [18–22]. It should then be feasible to detect the linear quadrupole response once its symmetry-dependent signature is explored and understood.

We start with a full linear polarization as follows:

$$P_{\alpha}^{(1)} = \chi_{D,\alpha\beta}^{(1)} E_{\beta} + \chi_{M,\alpha\beta}^{(1)} B_{\beta} + \chi_{Q,\alpha\beta\gamma}^{(1)} \nabla_{\beta} E_{\gamma} + \chi_{MQ,\alpha\beta\gamma}^{(1)} \nabla_{\beta} B_{\gamma}. \quad (1)$$

The first term yields the usual dielectric tensor of first rank. It includes magneto-optic effects if a magnetization or a dc magnetic field is present. The second term is a first rank linear response to the magnetic part of the applied electromagnetic wave and has been ignored so far as well. Its effect is weaker than the first term by the ratio of the electron velocity to the speed of light, i.e., by a factor of 100. The third term is a linear quadrupole response to the gradient of the electric field—the term of interest in this work. Being an optical response of second rank, it is symmetry dependent just as a third rank optical second-harmonic generation. Being a second rank optical process, the linear quadrupole response is non-vanishing only in materials lacking an inversion center. The fourth term is another linear quadrupole response but to the gradient of the magnetic field. It is weaker than the third term by a factor of 1000, and we will not consider it further.

Consider a GaAs crystal with a T_d symmetry. Its usual linear dielectric tensor is a unity tensor or a unity matrix multiplied by a scalar dielectric constant ϵ . Such a tensor reveals nothing about the crystalline symmetry of GaAs, as if the latter may just as well be an isotropic material. In fact the dielectric tensor of GaAs is indistinguishable from that of Si, which has a different cubic symmetry O_h . One manifestation of such an “isotropic” dielectric tensor is that the optical reflection from a GaAs or Si surface is not expected to change with the azimuthal orientation about the normal of the sample surface. When the linear quadrupole response is taken into consideration, GaAs starts to behave differently from Si. The centrosymmetric Si crystal has no linear quadrupole response. The GaAs crystal on the other hand has no inversion center, and thus its linear quadrupole response is non-vanishing. The latter is characterized by one susceptibility element [3]. We show that on a GaAs(100) surface, this quadrupole response yields an extra reflection that varies with the azimuthal orientation of the surface. Let the laboratory x axis and y axis overlap with (100) and (010) axes of a GaAs(100) wafer. Let the z axis be along the (001) axis pointing into the sample. In this coordinate frame, the third term in Eq. (1) is expressed as follows:

$$\delta P_x^{(1)} = i\chi_{Q,xzx}^{(1)} k_x E_y, \quad (2a)$$

$$\delta P_y^{(1)} = i\chi_{Q,xzx}^{(1)} (k_z E_x + k_x E_z), \quad (2b)$$

$$\delta P_z^{(1)} = i\chi_{Q,xzx}^{(1)} k_x E_y. \quad (2c)$$

Let $d_{14} \equiv \chi_{Q,xzx}^{(1)}$. When the sample subsequently rotates about the z axis by an azimuth θ , Eq. (2) becomes

$$\delta P_x^{(1)} = id_{14} [k_z E_y \cos 2\theta + (k_x E_x + k_x E_z) \sin 2\theta], \quad (3a)$$

$$\delta P_y^{(1)} = id_{14} [(k_z E_x + k_x E_z) \cos 2\theta - k_z E_y \sin 2\theta], \quad (3b)$$

$$\delta P_z^{(1)} = id_{14} k_x (E_y \cos 2\theta - E_x \sin 2\theta). \quad (3c)$$

At normal incidence with $k_x = 0$ and $k_z = k$, we have a modified dielectric tensor:

$$\overleftrightarrow{\epsilon} = \begin{pmatrix} \epsilon + id_{14}k \sin 2\theta & id_{14}k \cos 2\theta & 0 \\ id_{14}k \cos 2\theta & \epsilon - id_{14}k \sin 2\theta & 0 \\ 0 & 0 & \epsilon \end{pmatrix}. \quad (4)$$

The extra tensor elements modify the usual reflection coefficients for s - and p -polarized light. If we use the reflection matrix to relate the incident and reflected electric fields for s and p polarization [23],

$$\begin{pmatrix} E_s^{(r)} \\ E_p^{(r)} \end{pmatrix} = \begin{pmatrix} r_{pp} & r_{ps} \\ r_{sp} & r_{ss} \end{pmatrix} \begin{pmatrix} E_s^{(inc)} \\ E_p^{(inc)} \end{pmatrix}, \quad (5)$$

it can be readily shown that [24]

$$\begin{pmatrix} r_{pp} & r_{ps} \\ r_{sp} & r_{ss} \end{pmatrix} = \begin{pmatrix} r_0 - a * \sin 2\theta & -a * \cos 2\theta \\ -a * \cos 2\theta & r_0 + a * \sin 2\theta \end{pmatrix}. \quad (6)$$

Here $r_0 = (\sqrt{\epsilon} - 1)/(\sqrt{\epsilon} + 1)$ is the Fresnel coefficient of GaAs at normal incidence from air without the quadrupole response, and $a = id_{14}(2\pi/\lambda)\epsilon/(\sqrt{\epsilon} + 1)^2$.

The azimuth-dependent correction to the linear optical reflection can be observed with a normal-incidence reflectivity difference setup as illustrated in Fig. 1.

A p -polarized He–Ne laser beam with a diameter of 2 mm and a power of 500 μ W passes through a photo-elastic modulator (PEM) with its fast axis set at 45° and adding a time-varying phase $\Phi(t) = \Phi_0 \cos(2\pi ft)$ between the fast axis and the slow-axis components at $f = 50$ kHz. We use $\Phi_0 = \pi/2$. It is then incident on the sample near normal incidence. The reflected beam is detected with a Si PIN photo-receiver and the phase-sensitive analyzer (i.e., lock-in amplifiers). The first and second harmonics of the detected reflection are given respectively as follows [24]:

$$I(f) = 4 * I_{inc} * |r_0|^2 * J_1(\Phi_0) * \text{Re}\{a/r_0\} * \cos 2\theta, \quad (7a)$$

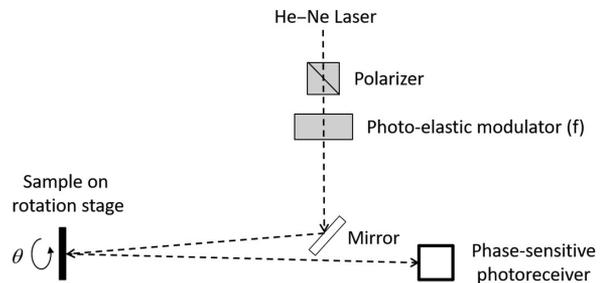


Fig. 1. Optical setup for measuring normal-incidence reflectivity difference between two orthogonal, linear polarizations as a function of azimuth orientation of the sample. The sample is either a GaAs(100) wafer or a Si(100) wafer.

$$I(2f) = 4 * I_{inc} * |r_0|^2 * J_2(\Phi_0) * \text{Re}\{a/r_0\} * \sin 2\theta. \quad (7b)$$

$J_1(\Phi_0)$ and $J_2(\Phi_0)$ are Bessel functions of the first kind. We measure $I_{inc} * |r_0|^2$ separately and in turn determine $\text{Re}\{a/r_0\} \cos 2\theta$ and $\text{Re}\{a/r_0\} \sin 2\theta$.

Figure 2 shows measured $I(f)$ and $I(2f)$ from a GaAs(100) wafer in air after normalization with $c'I_{inc}$. Both harmonics exhibit components that vary with the azimuth θ with magnitudes in the range of 10^{-3} , as we have anticipated a linear quadrupole response. Furthermore, the first harmonic indeed varies as prescribed in Eq. (7a), and the second harmonic varies as $\sin 2\theta$, again in agreement with Eq. (7b). For comparison (negative control), we measured the first and second harmonics from a Si(100) wafer and the results are displayed in Fig. 3 over the same signal range. Now neither harmonic shows a sign of azimuth dependence, consistent with the fact that the Si sample has an inversion center and thus possesses no linear quadrupole response.

We discuss the significance of the work presented so far. It is clear that the linear electric quadrupole response exists for crystalline materials lacking an inversion center, albeit 1000-fold weaker than the leading electric dipole response. As a higher ranked dielectric process though, the quadrupole response is more symmetry sensitive than the dipole response. It reveals the symmetry of a material as much as the second rank second-order nonlinear optical response. By measuring the azimuth dependence of $I(f)$ and $I(2f)$ at oblique incidence as well as normal incidence, one can distinguish crystals from different crystalline classes and, more importantly, different groups within same crystalline class (we will describe in detail in a separate, long

report [24]). As we demonstrated in this work for a normal-incidence reflectivity difference detection (Fig. 1) and Zhu and coworkers have reported extensively for oblique-incidence reflectivity difference detection [18–22,25], the leading-order dipole response is suppressed in these reflectivity difference detection schemes, as illustrated in Eq. (7) and in Figs. 2 and 3. In practice we should point out that unlike GaAs(100) and Si(100) wafers that we investigated here, surfaces of many crystalline samples may consist of an ensemble of single domains that are smaller than a few mm across and have different orientations, as encountered by Zhao and coworkers [14]. If one does not focus the illumination beam on a single domain, the azimuth dependence of the linear quadrupole response may be averaged out as if they do not exist. For this reason, it is best to measure $I(f)$ and $I(2f)$ in a microscopic configuration to ensure that only the response for a single domain is interrogated. The advantage of using a linear quadrupole response to determine crystalline phases and study phase transition, to the extent they exhibit characteristic azimuth dependence, is that it is simple and can be done with such low optical powers that do not raise the electron temperature over 1 K. Of course, for crystalline materials possessing inversion centers, the linear electric quadrupole response vanishes. In these cases, one can fall back to the second-order quadrupole responses. For non-central symmetric crystals that are anisotropic, the leading-order electric dipole response already yields an azimuth-dependent signal. The latter can overwhelm the signal from the electric quadrupole response. In these cases, the second-order electric quadrupole response suffers equally in the presence of an azimuth-dependent, second-order electric dipole response. We note here that the hidden phase of Sr_2IrO_4 that breaks the inversion symmetry should yield an observable azimuth-dependent linear optical response that is absent when the crystal is not in such a phase.

In summary, we uncovered the linear quadrupole response of a material to an electromagnetic wave and demonstrated its utility in revealing the crystalline symmetry of the material. In a way, it completes the description of optical responses to symmetry properties of materials. Though the magnetic dipole response [the second term in Eq. (1)] is also included in this uncovering effort, it is a dielectric process of second rank and reveals no new information on crystalline symmetry of the material except for contributing an isotropic signal that is 100-fold weaker.

Acknowledgment. X. D. Z. acknowledges support in the form of a Visiting Lecture Professorship and a Fudan Fellow from Fudan University.

Disclosures. The authors declare no conflicts of interest.

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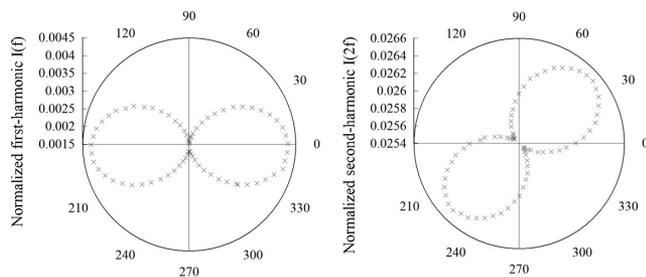


Fig. 2. Linear electric quadrupole response versus azimuth orientation from GaAs(100). Left panel: measured first-harmonic $I(f)$ normalized by $I_{inc}|r_0|^2$ versus azimuth θ from a GaAs(100) wafer in air. Right panel: second-harmonic $I(2f)$ after normalization by $I_{inc}|r_0|^2$ versus θ measured from the GaAs(100) wafer.

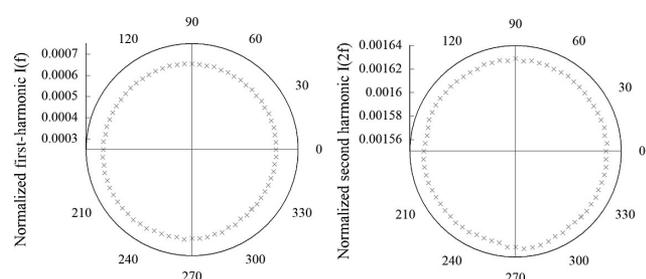


Fig. 3. Lack of linear electric quadrupole response from Si(100). Left panel: first-harmonic $I(f)$ normalized by $I_{inc}|r_0|^2$ versus azimuth θ measured from a Si(100) wafer in air. Right panel: second-harmonic $I(2f)$ after normalization by $I_{inc}|r_0|^2$ versus θ from the Si(100) wafer.

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