NONLINEAR OPTICS IN A ONE-DIMENSIONAL PERIODIC MEDIUM

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by

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Recently, intense research effort has been devoted to the development of solids with a prescribed one-dimensional periodic structure, known as superlattice. A medium with a superlattice can have very interesting optical and transport properties. In this section, we shall discuss some simple nonlinear optical effects in such a medium.

Wave propagation in a periodic structure is of course a well-known problem in solid-state physics. There, we deal with electron waves in a periodic lattice. The electron wave function takes the Bloch form $u(z) \exp(ikz-i\omega t)$ with $u(z) = u(z+d)$, where $d$ is the period of the lattice. If the Bragg condition for reflection is approximately satisfied, then propagation of the electron wave in the lattice becomes forbidden. This corresponds to the forbidden energy gap in the electron band structure. For electron-electron scattering in a periodic lattice, the crystal momentum defined as $G = \frac{2\pi}{d}$ can participate in momentum matching. The process is then known as an Umklapp process. All of these facts, true for electron waves, are also true for optical waves in a superlattice.

For nonlinear optics in a superlattice, the effect of the lattice periodicity is not so much on the strength of the wave interaction but rather on the phase matching condition. With the help of the crystal momentum, it is now possible to achieve the otherwise impossible collinear phase matching in a medium. For example, in second-harmonic generation, we can have the phase matching condition

$$|k(\omega)| \pm |k(\omega)| = \pm |k(2\omega)| + nG$$

(1)
where \( n \) is an integer, and \( +|k| \) and \( -|k| \) refer to forward and backward wave propagation respectively. Equation (1) indicates that by properly adjusting the value of \( G \), we can now have phase-matched second-harmonic generation with not only fundamental and second-harmonic beams in the same direction, but also fundamental and second-harmonic beams in opposite directions, or two fundamental beams in opposite directions. In analog to the electron case, these processes with \( n \neq 0 \) can be called coherent optical Umklapp processes.

We now give a more formal derivation of the effect. Assume a super-lattice with a linear dielectric constant \( \varepsilon(z) \) and a second-order non-linear susceptibility \( \chi^{(2)}(z) \) given by

\[
\varepsilon(z) = \varepsilon(z+d) = \sum_n \varepsilon_n \exp(inGz)
\]

\[
\chi^{(2)}(z) = \chi^{(2)}(z+d) = \sum_n \chi_n^{(2)} \exp(inGz). \tag{2}
\]

If \( \chi^{(2)} = 0 \), the fields at \( \omega \) and \( 2\omega \) should have the Bloch form

\[
E(\omega) = u_1(z) \exp[ik_1z - i\omega t]
\]

\[
E(2\omega) = u_2(z) \exp[ik_2z - 2i\omega t] \tag{3}
\]

where

\[
u_j(z) = \sum_n A_{jn} \exp(inGz). \tag{4}
\]

The wave vector \( k_j \) and the coefficients \( A_{jn} \) (normalized to \( A_{j1} \)), obtained from the solution of the wave equation, are functions of \( \omega \), \( d \), and \( \varepsilon_n \).
With $\chi^{(2)} \neq 0$, we can still let $E(\omega)$ and $E(2\omega)$ have the form of Eq. (3), but $A_n$'s are now slowly varying functions of $z$ as a result of nonlinear wave interaction. Second-harmonic generation is described by the wave equation

$$\left[-\frac{\partial^2}{\partial z^2} + \left(\frac{2\omega}{c}\right)^2 \varepsilon(2\omega,z)\right]E(2\omega) = -\frac{4\pi(2\omega)^2}{c^2} \chi^{(2)}(2\omega,z)E^2(\omega).$$

Substituting the expressions of Eqs. (2)-(4) into Eq. (5) and neglecting the $\partial^2 A_n/\partial z^2$ terms, we obtain
where $k_1$ and $k'_1$ (\(|k_1| = |k'_1|\)) are the wave vectors of the two fundamental waves. We are interested in the second-harmonic generation near phase matching such that

$$\Delta k = k_1 + k'_1 - k_2 - nG \sim 0.$$  

From Eq. (6.), if we neglect the non-phase-matched terms and the depletion of the fundamental waves, then we find

$$\frac{\partial A_{2n}}{\partial z} = \frac{16\pi\omega^2}{c^2} \sum_{n_c, n_d, n_e} (2\omega) A_{2n} e^{i[(k_1 + k'_1)(n_c + n_d + n_e)G]z}$$

where $k_1$ and $k'_1$ (\(|k_1| = |k'_1|\)) are the wave vectors of the two fundamental waves. We are interested in the second-harmonic generation near phase matching such that

$$\Delta k = k_1 + k'_1 - k_2 - nG \sim 0.$$  

For different $n_a$, Eq. (7.) forms a set of coupled equations from which we can solve for $A_{2n_a}(z)$, subject to the appropriate boundary conditions.

The general solution of Eq. (7.) is difficult, but it does lead to a general conclusion. If $\varepsilon_o > \varepsilon_1 > \varepsilon_2 > ...$ and $\chi_o^{(2)} > \chi_1^{(2)} > \chi_2^{(2)} > ...$, and if $|k|$ is not very close to $G/2$ such that $A_0 > A_1 > A_2 > ...$, then from Eq. (7), the phase-matched second-harmonic generation decreases as $n$ increases. In other words, $n$ acts as a measure of the perturbation order.
If \( \varepsilon(z) \) and \( \chi^{(2)}(z) \) are simple sinusoidal functions of \( z \), then the solution of Eq. (7) is readily obtainable. This has been done by Tang and Bey,\(^6\) although there is some question on whether the boundary conditions they used are correct. No such nonlinear optical experiment on artificial superlattice has yet been reported. There, however, exist in nature a number of substances which have built-in superlattice structure, for example, in crystals with periodic domains\(^8\) or rotational twinning.\(^9\) In those cases, the difficulty of quantitative analysis usually lies in the proper description of \( \varepsilon(z) \) and \( \chi^{(2)}(z) \). In addition, the periodicity of the superlattice is often not easily tunable. It turns out that there is a case where none of these difficulties arises. This is the case of third harmonic generation in cholesteric liquid crystals.\(^4\) (Inversion symmetry forbids second-harmonic generation for waves propagating along \( z \).) As we shall see, analytical solution of harmonic generation is available in this case and it provides an illuminating example for nonlinear optical effects in a superlattice.

In Fig. 1, we show the average molecular arrangement in a cholesteric liquid crystal. In a layer perpendicular to the \( z \) axis, the molecules are aligned parallel to the layer, but as the layer advances along the \( z \) axis, the direction of molecular alignment gradually rotates. Consequently, the medium has an overall helical structure. It corresponds to a one-dimensional periodic lattice with the period equal to half of the helical pitch \( p \). The most remarkable characteristic of cholesteric liquid crystals is that the helical pitch \( p \) can be easily adjustable from \( \pm 0.2 \mu m \) to several hundred microns by almost any external perturbation, such as temperature, pressure, and applied...
field.

Such a medium can be treated as a twisted birefringent material with a dielectric tensor

$$
\varepsilon(z) = \begin{pmatrix}
\varepsilon[1+\alpha\cos(4\pi z/p)], & \varepsilon\sin(4\pi z/p) & 0 \\
\varepsilon\sin(4\pi z/p), & \varepsilon[1-\alpha\cos(4\pi z/p)] & 0 \\
0 & 0 & \varepsilon_\eta
\end{pmatrix}
$$

(8)

where $\varepsilon = (\varepsilon_\xi + \varepsilon_\eta)/2$, $\alpha = (\varepsilon_\xi - \varepsilon_\eta)/2$, $\varepsilon_\xi$ and $\varepsilon_\eta$ are the principal dielectric constants in the directions parallel and perpendicular to the molecular alignment respectively. For this case, instead of using the Bloch-function formalism, it is actually much easier to solve the problem by a rotational transformation

$$
R(\theta=2\pi z/p) = \begin{pmatrix}
\cos\theta & \sin\theta & 0 \\
-s\sin\theta & \cos\theta & 0 \\
0 & 0 & 1
\end{pmatrix}
$$

(9)

which untwists the twisted helical structure. Then, in the rotating coordinate system, the medium appears as a simple birefringent material with a dielectric tensor

$$
\varepsilon_T = \varepsilon(z) : R^{-1} = \begin{pmatrix}
\varepsilon_\xi & 0 & 0 \\
0 & \varepsilon_\eta & 0 \\
0 & 0 & \varepsilon_\eta
\end{pmatrix}
$$

(10)

After the rotational transformation, the wave equation describing the third-harmonic generation is
\[
\left[ \frac{\partial^2}{\partial z^2} + \frac{4\pi}{p} \frac{\partial}{\partial z} - \left( \frac{2\pi}{p} \right)^2 + \frac{3\omega^2}{c^2} \epsilon_T(3\omega) \right] \cdot \hat{E}_T(3\omega) = -\frac{4\pi(3\omega)^2}{c^2} \hat{P}^{(3)}(3\omega) 
\]

\hspace{1cm} (11)

where

\[
\hat{\sigma} = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \hat{E}_T = R\hat{E}
\]

\[
\hat{P}^{(3)}(3\omega) = \chi^{(3)}_T : \hat{E}_T^3(\omega).
\]

\[
\chi_T = R : \chi^{(3)}(z) : R^{-1} \approx R^{-1} \approx 1
\]

is independent of \(z\) and has the form for a birefringent material such that we can write

\[
P^{(3)}_{T\xi}(3\omega) = C_{11}\epsilon^{3}(\omega) + C_{12}\epsilon^{2}(\omega)E^{2}(\omega)
\]

\[
P^{(3)}_{T\eta}(3\omega) = C_{21}\epsilon^{2}(\omega)E^{2}(\omega) + C_{22}\epsilon^{3}(\omega).
\]

Before solving Eq. (11), we should find the form of \(E_T(\omega)\) and \(E_T(3\omega)\) in linear propagation. This can be obtained by solving Eq. (12) with \(P^{(3)} = 0\). We find
\[ E_T(\omega) = [\hat{\epsilon}_+ e^{iK_z^+ z} + \hat{\epsilon}_- e^{-iK_z^- z}] e^{-i\omega t} \]

\[ \kappa_\pm(\omega) = (\omega - 1/c) m_\pm \]

\[ m_\pm = (\lambda_r^2 + 1) \pm (4\lambda_r^2 + \alpha^2)^{1/2} \]

\[ \lambda_r = 2\pi c/\omega p e^{-1/2} \]

\[ \hat{\epsilon}_\pm = [1/(1 + |f_\pm|^2)^{1/2}](\xi + i\tilde{f}_\pm \tilde{n}) \]

\[ f_\pm = 2m_\pm \lambda' / [m_\pm^2 + \lambda'^2 + (\alpha - 1)]. \] (13)

In the lab coordinates, the field becomes

\[ \vec{E}_\pm(\omega) = \vec{R}^{-1} \cdot \vec{E}_T(\omega) \]

\[ = \frac{1}{2} \xi_\pm [(\hat{x} + i\hat{y})(1 + f_\pm) + (\hat{x} - i\hat{y})(1 - f_\pm)] e^{i4\pi z/p} \]

\[ \exp[i(\kappa_\pm^2 - 2\pi/p)z - i\omega t]. \] (14)

Compared with the Bloch form in Eq. (3), we immediately recognize that

\[ k_\pm + nG = \kappa_\pm^2 - 2\pi/p \] (15)

where \( n \) is an integer, \( G = 4\pi/|p| \), and \( |k_\pm| \ll 2\pi/p \).

We can now solve Eq. (11) by letting \( \vec{E}_T(3\omega) \) have the form of

Eq. (13) with \( \tilde{\epsilon}_+ \) and \( \tilde{\epsilon}_- \) being slowly varying functions of \( z \). Following
the usual approximation, the solution is straightforward. Under the
near phase-matching condition
we find in the rotating coordinate system the output third-harmonic amplitude as

\[ \mathcal{E}_+^{(3\omega)} = 4\pi \left( \frac{\omega}{c} \right)^2 \left( \begin{array}{cc} D^+ & B^+ \\ A^+ & C^+ \end{array} \right) \cdot \chi_T^{(3)} \cdot e_m^+ e_n^+ \cdot \mathcal{E}_m^{(\omega)} \mathcal{E}_n^{(\omega)} \]

\[ \times \frac{1}{\Delta \pm \lambda_{mn}} \left\{ e^{i\Delta \mp \lambda_{mn} z^+} K_1 \right\} \]

\[ \mathcal{E}_-^{(3\omega)} = 4\pi \left( \frac{\omega}{c} \right)^2 \left( \begin{array}{cc} D^- & B^- \\ A^- & C^- \end{array} \right) \cdot \chi_T^{(3)} \cdot e_m^- e_n^- \cdot \mathcal{E}_m^{(\omega)} \mathcal{E}_n^{(\omega)} \]

\[ \times \frac{1}{\Delta \mp \lambda_{mn}} \left\{ e^{i\Delta \pm \lambda_{mn} z^-} K_2 \right\} \]  

(17)

where

\[ A = 2i\kappa_+ + (4\pi/p)\hat{e}_+^+ (4\pi/p)\hat{e}_+^* \]

\[ B = \hat{e}_+^+ [2i\kappa_+(4\pi/p)\hat{e}_+] \cdot \hat{e}_- \]

\[ C = \hat{e}_-^+ [2i\kappa_+(4\pi/p)\hat{e}_+] \cdot \hat{e}_+ \]

\[ D = 2i\kappa_+ + (4\pi/p)\hat{e}_-^+ \cdot \hat{e}_- \]

and \( K_1 \) and \( K_2 \) are constants determined by the boundary conditions. The third-harmonic output intensity is given by the Poynting vector

\[ S_{\pm}^{(3\omega)} = \left( \mid \mathcal{E}_\pm \mid^2 c \right) \frac{\text{Re}[q^+ |f|^2 / q]^\pm}{1 + |f|^2} \frac{\text{Re}[q^+ |f|^2 / q]^\pm}{1 + |f|^2} \]

\[ q^\pm = m^2 c^{1/2} \lambda^1 f^\pm. \]

Let us now discuss in more detail about the phase matching condition. Substitution of Eq. (15) into Eq. (16) gives, for perfect phase matching.
Note that $|k| < 2\pi/p$ is the wave vector of the optical Bloch wave in Eq. (3). Equation (19) shows that allowing $k$ to be either positive or negative for forward and backward propagation respectively, and having $nG$ adjustable, we can in general find 15 different phase-matching conditions. If $k$ is far from satisfying the Bragg condition such that

$$\lambda' \gg \alpha' \quad \text{and} \quad (1-\lambda') \gg \alpha^2/4\lambda',$$

then we have $k_\pm(\omega) = k_0(\omega) + n_\pm G$, where $k_0(\omega) = \omega / c$ is the wave vector when the medium is in the isotropic phase. The phase matching conditions become

$$\pm |k_0(\omega)| \pm |k_0(\omega)| \pm |k_0(\omega)| = \pm |k_0(3\omega)| + nG. \quad (20)$$

This shows explicitly how an adjustable crystal momentum $G$ can be used to compensate the phase mismatch between the fundamental and the third-harmonic waves. The value of $G$ needed to satisfy Eq. (19) or Eq. (20) can be easily estimated (given $n$) knowing the linear dielectric tensor for the medium.

We can divide the phase-matching conditions in Eq. (19) or Eq. (20) into three groups: a) $E(\omega)$ and $E(3\omega)$ are propagating in the same direction. In this case, $|k_0(3\omega) - 3k_0(\omega)| = G$ is small and the corresponding helical pitch $p$ is long. b) $E(\omega)$ and $E(3\omega)$ are propagating in opposite directions. A very short pitch $p$ is necessary to compensate the large phase mismatch $|k_0(3\omega) + 3k_0(\omega)|$. c) Two fundamental waves are propagating in opposite directions. The pitch $p$ for phase matching

$$k_\pm(\omega) + k_\pm(\omega) + k_\pm(\omega) = k_\pm(3\omega) = nG. \quad (19)$$
is also short since the mismatch \( |k_o(3\omega) \pm k_o(\omega)| \) is large.

Phase-matched third-harmonic generation in cholesteric liquid crystals has been studied experimentally by Shelton and Shen. Using mixtures of cholesteryl carbonate, cholesteryl nonanoate, and cholesteryl chloride, they found good agreement between experimental results and theoretical predictions from Eq. (19) or Eq. (20). Temperature tuning of the helical pitch was used in the experiment to achieve phase matching. Some of the predicted and observed phase-matching conditions are given in Table I. The phase-matching curve of \( 3k_+(\omega) = k_+(3\omega) \) is shown in Fig. 2 as an example. The cholesteric liquid crystal mixture changes from left to right helicity as the temperature increases around 52°C. The low-temperature and the high-temperature peaks in the figure correspond respectively to phase matching in left and right helical structure. Note that the observed peaks have a width of about ~ 0.2°C. Without the accurate theoretical predictions, it would be quite difficult to find these peaks experimentally.

The above formalism is of course also valid for other wave-mixing problems. No other nonlinear optical effects in a superlattice have even been discussed in the literature. Presumably, using the Bloch wave functions, one can treat these problems essentially in the same way as one would do with homogeneous media. As an example, let us consider stimulated Raman scattering in a superlattice. The wave equation for Stokes wave should have the form

\[
[- \frac{\partial^2}{\partial z^2} + \frac{\omega_s^2}{c^2} \varepsilon_{s, \text{eff}}(z)]E_s(z) = 0
\]
where
\[ \varepsilon_{s,\text{eff}}(z) = \varepsilon_s(z) + \chi_R^{(3)}(z) |E_\lambda(z)|^2 \]
\[ = \varepsilon_{s,\text{eff}}(z+d) \]
\[ |E_\lambda(z)|^2 = u_\lambda^2(z) = u_\lambda^2(z+d) \]
assuming negligible depletion of \( |E_\lambda(z)|^2 \). We can then express \( E_s(z) \) also in the Bloch form
\[ E_s(z) = u_s^2(z) \exp(i k_s z - i \omega_s t). \]
The eigenvalue \( k_s \) can be solved from Eq. ( ) by expanding all the periodic functions into Fourier series and substituting them into Eq. ( ). For stimulated Raman scattering, \( k_s \) is expected to have a negative imaginary part.

ACKNOWLEDGMENT

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<table>
<thead>
<tr>
<th>Phase Matching Condition</th>
<th>Predicted pitch for phase matching (m)</th>
<th>Predicted temperature for phase matching (°C)</th>
<th>Observed temperature for phase matching (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3k_+(\omega)=k_+(3\omega)-G$, $3k_o(\omega)=k_o(3\omega)-G$</td>
<td>-17, +17</td>
<td>49.4, 54.2</td>
<td>49.3, 54.1</td>
</tr>
<tr>
<td>$3k_-(\omega)=-k_-(3\omega)+G$, $3k_o(\omega)=-k_o(3\omega)+2G$</td>
<td>0.47</td>
<td>38.2</td>
<td>38.1</td>
</tr>
<tr>
<td>$2k_+(\omega)-k_-(3\omega)$, $2k_o(\omega)-k_o(3\omega)=k_o (3\omega)-2G$</td>
<td>1.4</td>
<td>33.3</td>
<td>33.6</td>
</tr>
<tr>
<td>$-k_+(\omega)+2k_-(\omega)=-k_-(3\omega)$, $-k_o(\omega)+2k_o(\omega)=-k_o (3\omega)+2G$</td>
<td>0.7</td>
<td>31.1</td>
<td>31.2</td>
</tr>
</tbody>
</table>

Table I. Phase Matching Conditions for Third-harmonic Generation in a Mixture of Cholesteric Liquid Crystals.

Generation in a Mixture of Cholesteric Liquid Crystals.
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FIGURE CAPTIONS

Fig. 1 Sketch of molecular alignment in a cholesteric liquid crystal
displacing the helical structure.

Fig. 2 Normalized third-harmonic generation versus temperature near
phase matching in a mixture of 1.75 cholesteryl chloride and
1.00 cholesteryl Myristate. The peak at lower temperature
(corresponding to left helical structure) is generated by
right circularly polarized fundamental waves and the one at
higher temperature (corresponding to right helical structure)
is generated by left circularly polarized fundamental waves.
The solid line is the theoretical phase matching curve and the
dots are the experimental data points. (after J. W. Shelton
Fig. 1
Normalized third harmonic intensity vs. T (°C)
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