

Photogalvanic Effects in Heteropolar Nanotubes

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We show that an electrical shift current is generated when electrons are photoexcited from the valence to conduction bands on a BN nanotube. This photocurrent follows the light pulse envelope and its symmetry is controlled by the atomic structure of the nanotube. We find that the shift current has an intrinsic quantum mechanical signature in which the chiral index of the tube determines the direction of the current along the tube axis. We identify the discrete lattice effects in the tangent plane of the tube that lead to an azimuthal component of the shift current. The nanotube shift current can lead to ultrafast optoelectronic and optomechanical applications.

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Recent progress in synthesis of nanometer scale materials has led to the discovery of $B_xC_yN_z$ nanotubes. They can be formed in nearly homogeneous ordered structures [1,2] or in multiwall hybrid structures with alternating BN and C compositions [3]. These materials differ fundamentally from the structurally similar carbon nanotubes by being *noncentrosymmetric* (NCS) and *polar*. This opens the possibility for accessing a new class of photovoltaic effects at the molecular scale.

Photovoltaic effects in NCS materials are often based on an asymmetric generation of hot carriers at momenta $\pm\mathbf{k}$ leading to a so-called “ballistic photocurrent” [4–6]. In polar NCS materials, photoexcitation across the band gap with polarized light also produces the so-called electrical “shift current” [7–9]. Microscopically this originates from a net displacement of charge in the unit cell due to light induced interband transitions (\mathbf{J}_e), intraband relaxation (\mathbf{J}_s), and (radiative) transitions to the original bands (\mathbf{J}_r). In bulk materials, the excitation component \mathbf{J}_e usually prevails.

We show that *unpolarized light* can induce a shift current \mathbf{J}_e in polar NCS nanotubes, with a direction along the tube axis which is determined by the chiral index of the tube. We find that this effect has an essentially quantum mechanical origin, where the *sign* of the current along the tube axis is controlled by the phase matching of electronic Bloch waves around the tube circumference. The discrete lattice structure controls the azimuthal component of this current and thus produces a net *helical current* on the tube. These photoeffects can lead to an assortment of new optoelectronic, optomechanical, and magnetic applications, and interesting extensions to ring structures [10] and heterojunctions [11]. We should stress that the photoeffects we discuss here are found at nonlinear order in the exciting fields, and are therefore physically distinct from chiral currents tilted with respect to the tube axis, predicted in dc

bias driven chiral BN nanotubes [12] or chiral stretched C nanotubes [13,14].

A flat BN sheet has a honeycomb lattice with the B and N occupying alternate sublattices as shown in Fig. 1. The physics of the shift current can be understood qualitatively by considering the response of this 2D network of bonds to normally incident polarized light. The valence states are polarized towards the N sites and the conduction states towards the B sites. For vertically polarized (*y*-polarized) incident light the response of the system is dominated by the bonds which produce a net *y*-polarized current. For horizontally (*x*-polarized) incident light, the bonds with a nonzero horizontal component dominate, but these also produce a net *y*-polarized current. Note that excitation with an unpolarized incident field *cannot* produce a net current on this lattice since it has a threefold symmetry. However, this symmetry is removed when the sheet is wrapped into a cylindrical nanotube where the physics should be dominated by excitations with the field polarized along the tube axis. Depending on the wrapped structure of the tube, we anticipate an intrinsic photocurrent which can flow along the tube, around the tube, or in a chiral pattern on the tube surface.

These ideas can be quantified by developing a quantum mechanical model which generalizes our long wavelength theory for a nonpolar carbon nanotube [15] to the heteropolar lattice. We work in a basis of Bloch orbitals $\Phi_{k\alpha}(r) = e^{ik\cdot r} \sum_n e^{-ik\cdot(r-R_n-\tau_\alpha)} \phi_{n\alpha}/\sqrt{N} = e^{ik\cdot r} U_{k\alpha}$ where $\alpha = \pm 1$ denotes the two sublattices occupying sites at τ_α in the *n*th unit cell. We study the states near the conduction and valence band edges at the *K* and *K'* points of the Brillouin zone shown in Fig. 1. A long wavelength Hamiltonian for these states is obtained by an expansion in small crystal momenta around these points, and yields in our two component basis ($\hbar = 1$)

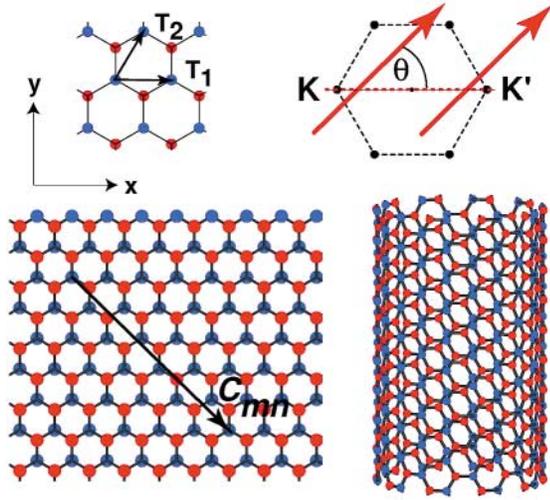


FIG. 1 (color). Planar BN forms a honeycomb lattice with B and N occupying alternate sites (upper left). A BN tube is formed by wrapping the sheet through the translation vector C_{mn} (lower left) quantizing the transverse crystal momenta. The upper right-hand panel shows two representative lines of allowed momenta for a tube with a nonzero chiral index $\nu = \text{mod}(m - n, 3)$ and chiral angle θ . The lower right panel shows the structure for the nonchiral armchair (10, 10) wrapping of the BN sheet.

$$H_{\lambda}(\Delta, k, \delta_{\lambda}) = \begin{pmatrix} \Delta & \lambda v_F(k - i\delta_{\lambda}) \\ \lambda v_F(k + i\delta_{\lambda}) & -\Delta \end{pmatrix}, \quad (1)$$

where $\lambda = \pm 1$ is an index which labels an expansion around the K or K' points. The Hamiltonian in Eq. (1) is parametrized by three energies: a symmetry breaking site diagonal potential Δ , the kinetic energy $v_F k$ for motion along the tube, and the kinetic energy $v_F \delta$ due to the quantization of the transverse momentum around the circumference of the tube. On a cylindrical tube with lattice constant a and primitive lattice translation vectors in its tangent plane $T_1 = a(1, 0)$ and $T_2 = a(1/2, \sqrt{3}/2)$ (Fig. 1) it is conventional to index the lattice structure by two integers m and n which define a superlattice translation vector $C_{mn} = mT_1 + nT_2$. The transverse momenta on an (m, n) tube are quantized to the values $\delta_N = \delta_0 + 2\pi N/|C_{mn}|$ where $\delta_0 = 2\pi \text{sgn}(\nu)/3|C_{mn}|$, depending on the sign of the chiral index of the tube, $\nu = \text{mod}(n - m, 3)$. In Eq. (1) $\delta_{\lambda} = \lambda\delta_N$.

The eigenvectors of H in Eq. (1) are

$$g_v = \begin{pmatrix} ue^{-i\phi/2} \\ -ve^{i\phi/2} \end{pmatrix} \frac{e^{i\theta_{vk}}}{\sqrt{2}}; \quad g_c = \begin{pmatrix} ve^{-i\phi/2} \\ ue^{i\phi/2} \end{pmatrix} \frac{e^{i\theta_{ck}}}{\sqrt{2}}, \quad (2)$$

where $E = \sqrt{v_F^2(k^2 + \delta_N^2) + \Delta^2}$, $\phi = \tan^{-1}(\delta_N/\lambda k)$, $u = \sqrt{(E - \Delta)/E}$, and $v = \sqrt{(E + \Delta)/E}$. In the rest of this paper we will set the Fermi velocity $v_F = 1$ so that energies and momenta are measured in the same units. Equation (2) explicitly includes a gauge function θ_{mk} since the overall phase of the Bloch function is not

fixed, and our calculation will require differentiation with respect to k . The Bloch eigenfunctions of our problem are expressed as the product of three factors $\psi_{km}(r) = e^{ik \cdot r} \sum_{\alpha} g_{m\alpha}(k) U_{k\alpha}(r)$.

We extend the model Hamiltonian in Eq. (1) to include coupling of electrons to the oscillating optical fields $\mathbf{E}(t) = \mathbf{E}e^{-i\omega t} + \text{c.c.}$ through the dipole operator [8,9] $H_{\text{int}} = -e\mathbf{E}(t) \cdot \mathbf{r}$. For a field polarized along the tube direction the matrix elements of the dipole operator between band eigenstates m and m' at crystal momenta k and k' are expressed using a formulation due to Blount [16]

$$r_{m'm}(k', k) = \langle \psi_{k'm'} | r | \psi_{km} \rangle = -i \langle \psi_{k'm'} | \partial_k | \psi_{km} \rangle + i\delta(k - k') \sum_{\alpha\beta} \delta_{\alpha\beta} g_{m'\beta}^*(k') \partial_k g_{m\alpha}(k). \quad (3)$$

The second term on the right-hand side of (3) forms the connection $\xi_{m'm} = ig_{m'}^*(k) \cdot \partial_k g_m(k)$ due to the k dependence of the eigenstates in (2) [17].

In general the shift current \mathbf{J} can be expressed in terms of the band off-diagonal matrix elements of the velocity operator $\mathbf{v}_{\beta\alpha}$ ($\mathbf{v} = i[H, \mathbf{r}]$), and the band off-diagonal term in the density matrix $\rho_{\alpha\beta}$, calculated to second order in the exciting fields \mathbf{E} , as follows [7–9]:

$$\mathbf{J} = 2e \sum_{m \neq n} \int \frac{dk}{2\pi} \mathbf{v}_{mn}(k) \rho_{nm}(k) = \mathbf{J}_e + \mathbf{J}_s + \mathbf{J}_r. \quad (4)$$

We focus on the component of the excitation current J_e along the tube direction. After evaluating the sum in (4), we arrive at the transparent result

$$J_e = 2e \int \frac{dk}{2\pi} \dot{f}_{cv}(k) R_{cv}(k) \approx e\dot{n}\mathcal{R}. \quad (5)$$

Here $\dot{f}_{cv}(k)$ is the transition rate at wave vector k , and the shift vector $R_{cv}(k)$ is given by

$$R_{cv}(k) = \partial_k \theta_{vc}(k) + \xi_{cc}(k) - \xi_{vv}(k) \quad (6)$$

with $\xi_{vc}(k) = |\xi_{vc}(k)|e^{i\theta_{vc}(k)}$. The shift vector $R_{cv}(k)$ is invariant under the gauge transformations $\exp(i\theta_{mk})$ and we will evaluate it in a gauge with $\partial_k \theta_{mk} = 0$.

For an incident electric field polarized along the tube direction, interband excitations are allowed only between band states with the same transverse momentum δ . For transitions between the lowest two azimuthal subbands ($N = 0$) using the eigenfunctions in Eq. (2) we find

$$\xi_{vc}(k) = \frac{-1}{2} uv \left(\frac{\Delta}{E^2 - \Delta^2} \partial_k E + i\partial_k \phi \right), \quad (7)$$

which gives the off-diagonal contribution in Eq. (6)

$$\partial_k \theta_{vc} = \partial_k \tan^{-1} \left(\frac{-\delta \sqrt{\delta^2 + \Delta^2 + k^2}}{k\Delta} \right). \quad (8)$$

The diagonal elements in Eq. (6) are

$$\xi_{mm}(k) = ig_m^{\dagger} \cdot \partial_k g_m = \mp \frac{\Delta}{2E} \left(\frac{\delta}{\delta^2 + k^2} \right), \quad (9)$$

where the sign is negative for valence states and positive for conduction states. Combining Eqs. (8) and (9) we obtain the shift vector

$$R_{cv}(k) = \frac{2\delta\Delta}{(\delta^2 + k^2)\sqrt{\delta^2 + \Delta^2 + k^2}}. \quad (10)$$

Comparison with Eq. (9) shows that the shift current [Eq. (5)] opposes the direction of the ground state polarization of the tube.

This shift vector is odd in the symmetry breaking potential Δ and *odd in the transverse momentum* δ . Therefore, two BN tubes with nearly the same wrapped lattice structure but *opposite* chiral indices ν exhibit reversed ground state polarizations and opposite shift currents. Armchair BN nanotubes with wrapping indices (m, m) have chiral index $\nu = 0$ and do not exhibit a longitudinal shift current [as shown in the middle panel in Fig. 2 for the (5, 5) tube]. Zigzag BN tubes with wrapping indices $(m, 0)$ can be grouped into three families with positive, negative, or zero shift currents distinguished by the sign of the chiral index ν [an example for the (8, 0) tube with $\nu = -1$ is in the left panel of Fig. 2]. It is important to notice that an isolated flat BN sheet has a threefold symmetry axis perpendicular to the BN plane and therefore it has zero electric polarization in its tangent plane, by symmetry. Thus it has no shift current for excitations at the band edge. The nonzero shift vector in Eq. (10) when $k \rightarrow 0$ is a remarkable long wavelength quantum mechanical effect that reveals the quantization of the transverse momentum on the wrapped tube.

The shift current J_e in Eq. (5) is determined by the average shift vector \mathcal{R} , describing the change of polarity in the excitation, and by the carrier injection rate \dot{n} . The BN

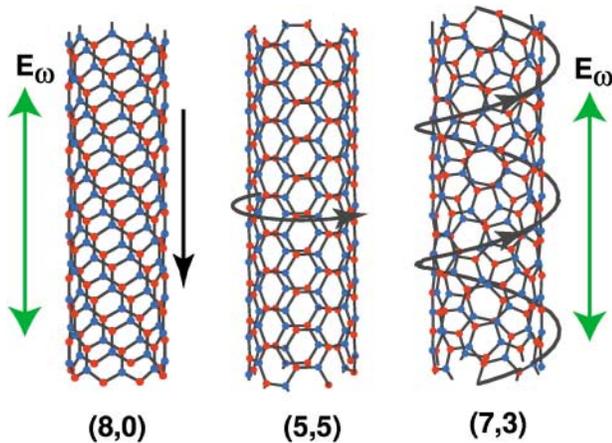


FIG. 2 (color). Electronic shift currents produced by excitation of BN nanotubes with light polarized along their axis. For the (8,0) wrapping the chiral index is $\nu = -1$, and the shift current is purely longitudinal. The (5,5) armchair wrapping has chiral index $\nu = 0$ and has zero longitudinal current and a nonzero azimuthal current which runs “counterclockwise” on the tube surface. The (7,3) wrapping has a chiral shift current with nonzero longitudinal and azimuthal components.

bond has significant ionic character with [18] $2\Delta \approx 4$ eV. This gives for excitations near the band edge, $k \rightarrow 0$, a shift vector with a magnitude $\mathcal{R} \approx 0.06$ nm for a (17, 0) tube. For an incident intensity $S = 100$ kW/cm² we can also obtain the interband excitation rate; we estimate that $\dot{n} \approx 70$ nm⁻¹ μ s⁻¹ produces a net electronic shift current of $J_e \approx 0.67$ pA. This value is slightly larger than what one obtains for excited bulk polar semiconductors. Opposing shift currents on different walls of a coaxial multiwall tube can reduce the macroscopic current, but cannot eliminate it except for rare high symmetry concentric lattice structures. We also expect that the recombination current J_r will oppose J_e since both currents rely on optical transitions with longitudinal polarization. However, this should not prevent the observation of J_e using pulsed laser excitation since the time scale for J_r is of the order of nanoseconds.

This formalism can be extended to study *chiral shift currents* with nonvanishing longitudinal and azimuthal components. Interestingly, the long wavelength Hamiltonian in Eq. (1) gives zero azimuthal current for *any* chiral index ν . As $Q_{\pm} = k \pm i\delta \rightarrow 0$ this occurs because of a cancellation of contributions from the K and K' points whose long wavelength Hamiltonians have opposite handedness. However, azimuthal currents arise due to discrete lattice effects occurring at higher orders in an expansion in Q_{\pm} . To study this, we define two unit vectors at each point in the tube surface, perpendicular to the local outward unit normal \hat{n} : \hat{e}_x which points along the tube axis, and $\hat{e}_y = \hat{n} \times \hat{e}_x$ which points counterclockwise on the tube surface. A chiral angle θ is defined as the angle between \hat{e}_x and the T_1 lattice direction as shown in Fig. 1 (with this convention armchair nanotubes have $\theta = 0$). Then the lowest nonvanishing contribution to an azimuthal (y -polarized) shift current must have the form $\cos(6\phi - 3\theta)$ where $\phi = \tan^{-1}(\delta/k)$. The dependence on 6ϕ means that azimuthal currents first occur in the continuum theory at sixth order in $|Q|$.

We can study these terms by replacing the kinetic energy terms in the Hamiltonian of Eq. (1) by the discrete lattice counterpart $iv_F(k + i\delta) = iv_F Q_{\pm} \rightarrow t \sum_n e^{i(K+Q)\cdot\tau_n}$ where t is the hopping amplitude between sites connected by the bond vectors τ_n . A systematic expansion of the azimuthal shift current in powers of Q_{\pm} then gives contributions with the correct lattice symmetry and shows that the ratio of the azimuthal and longitudinal in-plane current densities scales as

$$p = \frac{J_y}{J_x} = \frac{(k^2 + \delta^2)^3 \tau^3}{\delta(\Delta^2 + k^2 + \delta^2)} \cos(6\phi - 3\theta). \quad (11)$$

The azimuthal current for any zigzag wrapping is zero because of the angular factor, while its longitudinal current, shown in Fig. 2, is determined by the chiral index ν . For armchair tubes and all nonzigzag tubes with chiral index $\nu = 0$, we have $\delta = 0$, so the shift current is purely azimuthal with a direction determined by the sign of the

potential Δ . These energy dependent currents vanish at the band edge as $\propto(E^2 - \Delta^2)^3$. Nonzigzag tubes with chiral index $\nu \neq 0$ have a nonzero δ and thus the azimuthal current is nonzero with $p \propto (\delta/\Delta)^2(\delta\tau)^3$. There the shift current circulates in a *helical pattern* on the tube surface as shown in the right panel of Fig. 2, with a chirality determined by the index ν . The pitch is also energy dependent and increases according to $p(E) = p(0) + a(E^2 - \Delta^2)$. Thus, as shown in Fig. 2, the zigzag nanotubes generate a photocurrent like a wire, the armchair tubes like a coil, and the chiral tubes can exhibit a helical current on the tube surface.

Alternatively, the shift current can be studied in a semiclassical model, by considering an expansion in t/Δ , where t is the nearest neighbor hopping amplitude, and Δ is the site diagonal potential. In the limit $t/\Delta \ll 1$ the tube can be regarded as a network of independent bonds whose excitations are superimposed. Here the local symmetry of the zigzag tube requires zero net azimuthal current while the armchair wrapping has a nonzero azimuthal current with its direction determined by the sign of Δ . However, it is difficult to correctly describe the physics of the *longitudinal* current using this model. This is because the longitudinal current is controlled by the quantization of the transverse momentum δ . The first terms in the semiclassical expansion that are sensitive to δ occur at order $(t/\Delta)^N$ where N is the number of bonds (≈ 40) around the tube circumference. This reflects the fact that the longitudinal current is fundamentally a nonclassical quantity for this system.

The longitudinal shift current reduces the ground state electric polarization of the nanotube. This can lead to a *fast readjustment* of atomic positions on the tube walls. Generation of voltages by a mechanical elongation [19] of NCS nanotubes is a related effect. In both situations the response can be stronger in buckled nanotubes [20] or if different types of atoms occur in different layers, as in MoS₂, WS₂ [21], or GaSe nanotubes [22]. Recently, mechanical motions, strikingly similar to those found in some biomolecular systems [23], were observed in irradiated nanotube bundles [24]. Interesting mechanical response to an applied dc bias is observed in carbon nanotubes immersed in a solution of NaCl [25]. Here, the motion is caused by *attraction of ions* of a given polarity to the nanotube. The speed but short duration of the shift current-induced mechanical response complements the slow but steady state effect of a dc bias.

Experimental observation of the shift current in BN nanotubes would provide a striking illustration of fundamental concepts in the modern quantum theory of polarization. The effect is also promising for new applications since it couples the microscopic physics on short length

scales, which can be tuned by local fields and mechanical loads, to the long distance properties of the system (polarization, photovoltage, etc.) Finally, there is a rapidly growing family of related submicron one dimensional materials to which these ideas can be applied.

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