

Optical phonons in polar semiconductor nanowires

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We show that the long-range dipolar interactions in a crystalline cubic polar semiconducting nanowire give rise to an important splitting of the Raman-active transverse optic (TO) and longitudinal optic (LO) phonons at the center of the Brillouin zone. The dipole sums that determine the two LO and two TO phonon frequencies in the nanowire are sensitive to the aspect ratio (L/D), where L and D are the length and diameter, respectively. In the limit $L/D \rightarrow \infty$, we predict the phonon frequencies for several important polar semiconducting nanowires. Our calculated results are also compared with Raman scattering data obtained on crystalline GaP and GaAs semiconducting wires.

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Semiconducting nanowires have recently been shown to produce exciting devices, such as chemical sensors,¹ lasers,² and field effect transistors.³ With sufficiently small diameters ($D \leq 10$ nm) one expects quantum confinement to alter the device properties via the electronic and phonon states.^{4,5} Raman scattering has been used to study the effects of phonon confinement.^{6,7} In agreement with the model first proposed by Richter *et al.*⁸ and extended by Campbell and Fauchet,⁹ the nanowire Raman-active optical phonon line is found to downshift and broaden asymmetrically with decreasing wire diameter. Recent work has extended the Raman line shape analysis to include the diameter distribution of the nanowire sample.¹⁰ The essential ideas which evolved from Richter *et al.*'s model calculations for nanowires are the following: (1) a proper description of the long wavelength ($q=0$) phonon in the *nanowire* with a wire axis along the z direction requires a collection of *bulk* phonon states $\omega(q_{\perp})$ with wave vectors q_{\perp} in the range ($0 < q_{\perp} \leq 1/D$), where q_{\perp} is the wave vector along a direction perpendicular to z , and D is the diameter of the nanowire, and (2) one should expect first-order Raman scattering activity in the nanowire to extend over the range of phonon frequencies $\omega(0)$ to $\omega(0) + \Delta\omega$, where $\Delta\omega \approx (d\omega/dq_{\perp})(1/D)$. This phonon confinement or "size" effect on the Raman spectrum is expected to occur in both polar (e.g., GaAs, GaP) or nonpolar (e.g., Si, Ge) semiconducting nanowires.

In this Brief Report, we show that there is a second important effect on the Raman spectrum of a semiconductor nanowire that is of an altogether different origin. This "shape" effect stems from the long range dipolar interactions within the nanowire.¹¹ The parameters of the nanowire that determine the strength of this shape effect are the aspect ratio of the wire (L/D), the high frequency dielectric constant and the ion plasma frequency. Raman spectra on GaAs and GaP nanowires are presented and compared with theory. We report Raman spectra on long nanowires (lengths exceeding a few microns) with a most probable diameter $D \sim 20$ nm, where the quantum confinement or "size" effect is not important, i.e., the model of Richter *et al.* produces insignificant changes in the linewidth and peak position relative to that observed for the bulk. For these samples, we anticipate only a "shape" effect.

Theories of long-wavelength phonons in nanowires and superlattices have focused on the relevant boundary conditions.¹²⁻¹⁷ There are "mechanical" boundary conditions, since surface atoms have fewer "springs" to neighboring atoms. There are also changes in the electric and polarization forces due to the shape of the system. How one combines these effects has been debated.¹²⁻¹⁷ We show that the role of polarization forces can be determined in a simple way by evaluating the dipolar summations directly.

In the vibration of an optical phonon, the cations and anions oscillate out of phase and create oscillating dipoles. The dipoles interact by dipole-dipole interactions. The important term governing the dipole-dipole interactions is given by^{11,18}

$$T_{\mu\nu}(\mathbf{k}) = \sum_{j \neq \ell} e^{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_{\ell})} \phi_{\mu\nu}(\mathbf{R}_{j\ell}), \quad (1)$$

$$\phi_{\mu\nu}(\mathbf{R}) = \frac{\delta_{\mu\nu}}{R^3} - \frac{3R_{\mu}R_{\nu}}{R^5}, \quad (2)$$

where \mathbf{k} is the phonon wavevector and R_j are the ion coordinates. In three dimensions (i.e., isotropic shape), summation (1) is conditionally convergent and the answer is determined, in part, by physical considerations,¹¹

$$\lim_{k \rightarrow 0} T_{\mu\nu}(k) = \frac{4\pi}{V_0} \left[\frac{k_{\mu}k_{\nu}}{k^2} - \frac{1}{3} \delta_{\mu\nu} \right], \quad (3)$$

where V_0 is the volume of the unit cell. Also note that $Tr\{T_{\mu\nu}\} = 0$. Next, we describe how $T_{\mu\nu}(k)$ enters into the calculation of the phonon frequencies.

For a nanowire, the infinite part of the summation extends only along the z -axis (growth axis) of the wire, and the summation is absolutely convergent. We use a coordinate system $\mathbf{R}_j = (\vec{\rho}_j, z_j)$, where $\vec{\rho}_j$ is in the plane that forms the cross section of the nanowire, and we define $\mathbf{k} = (\mathbf{q}_{\perp}, k_z)$ where \mathbf{q}_{\perp} is the wave vector in the cross sectional plane. The summation over $\mathbf{R}_j \neq \mathbf{R}_{\ell}$ has a separate term for $\vec{\rho}_j = \vec{\rho}_{\ell}$. We find

$$T_{\mu\nu} = \frac{2}{a^3} [1 - 3\delta_{\mu=z}\delta_{\nu=z}] \Phi(ka) + \sum_{\rho_j \neq \rho_{\ell}} e^{i\mathbf{k} \cdot \mathbf{R}_j} \phi_{\mu\nu}(\mathbf{R}_{j\ell}), \quad (4)$$

$$\Phi(\theta) = \sum_{n=1}^{\infty} \frac{\cos(n\theta)}{n^3}. \quad (5)$$

At $\theta = ka = 0$, then $\Phi(0)$ is given by the Riemann zeta function $\zeta(3) = 1.2020$, and $\Phi(\pi) = -3\zeta(3)/4$. The second term in Eq. (4) can be evaluated by Ewald-type summation using the Bessel function $K_0(z)$. Define $p_\alpha = k + 2\pi m/a$, where a is the spacing between planes along the axis of the nanowire. Specific tensor components of $T_{\mu\nu}(k)$ are

$$T_{zz} = -\frac{4}{a^3}\Phi(\theta) + \frac{2}{a^3} \sum_{m, \rho_j \neq \rho_\ell} e^{i\mathbf{q} \cdot (\rho_j - \rho_\ell)} (p_m a)^2 K_0(p_m \rho_{j\ell}), \quad (6)$$

$$T_{xx} = T_{yy} = \frac{2}{a^3}\Phi(\theta) + \frac{2}{a^3} \sum_{m, \rho_j \neq \rho_\ell} e^{i\mathbf{q} \cdot (\rho_j - \rho_\ell)} (p_m a)^2 \times \left[\frac{K_1(p_m \rho_{j\ell})}{p_m \rho_{j\ell}} - \frac{\rho_{x,j\ell}^2}{\rho_{j\ell}^2} K_2(p_m \rho_{j\ell}) \right]. \quad (7)$$

The above expressions have been evaluated numerically for several cubic lattices, in the limit that $\mathbf{k} \rightarrow 0$, we find $T_{zz} = -4\pi/(3V_0)$, $T_{xx} = T_{yy} = 4\pi/(6V_0)$. We presume the same result is found for other cubic lattices. Note that this is not the same as limit (3) for three dimensions. It was noted by Cohen and Keffer¹¹ that these limits should differ although they do not state the result for nanowires. The dipolar contribution to the LO and TO phonon frequencies is different in the nanowire compared to an infinite three-dimensional crystal. The length scale over which a dipole sum in a nanowire is significantly different from that in an infinite lattice is $kR \leq 10$.¹¹ Therefore, for an experiment done with visible light ($\lambda \sim 500$ nm), we expect the shape effect to be significant for nanowires with a diameter ≤ 5000 nm.

Why are the local fields for a cylinder different than for a sphere? We answer this question by doing a calculation along the lines of Cohen and Keffer.¹¹ We replace the lattice sum by a continuous integral over the volume, which should be accurate at a long wavelength. A spherical hole of radius b is omitted from the origin. For a cylinder of radius R and length $-L < z < L$, the dipole sum at the center, at zero wave vector, is given by the integral

$$T_{zz} = \frac{4\pi}{V_0} \left[\int_0^b dz \int_{\sqrt{b^2 - z^2}}^R \rho d\rho + \int_b^L dz \int_0^R \rho d\rho \right] \times \left(\frac{1}{[z^2 + \rho^2]^{3/2}} - \frac{3z^2}{[z^2 + \rho^2]^{5/2}} \right).$$

The integrals over $d\rho$ can be done easily, giving

$$T_{zz} = \frac{4\pi}{V_0} \left[\frac{2}{3} - \frac{L}{\sqrt{L^2 + R^2}} \right].$$

For a thin wire, with $L \gg R$, the result is that $T_{zz} = -4\pi/3V_0$, in agreement with our dipole sum. For a platelet, with $L \ll R$, the result is $T_{zz} = 8\pi/3V_0$, in agreement with classical physics. The dipolar sums are therefore strongly shape dependent.

An important feature of Eq. (6) is that the term $K_0(p_m \rho)$ vanishes very rapidly for large values of ρ . The summation $\rho_j \neq \rho_\ell$ requires only one or two shells of neighboring atoms in order to obtain numerical convergence. So all sites in the nanowire have approximately the same dipolar energies except those right on the surface layer. This conclusion agrees with the calculation¹⁹ of local fields in a crystal, where only the surface atoms “see” a local field which is different from the bulk.

We now apply these local field corrections to the optical phonons in a polar semiconductor nanowire ($L/D \rightarrow \infty$). The splitting between the optical phonons at a long wavelength is provided by the high frequency dipolar sums. It is important to do them including the background dielectric function of the ion cores. We can write the dispersion relation of an optical phonon in terms of the local spring constant (ω_0^2) and the local electric field (E_μ) as

$$\omega^2 q_\mu = \omega_0^2 q_\mu - \frac{e^*}{M} E_\mu, \quad (8)$$

$$E_\mu = -T_{\mu\nu} [e^* q_\nu + \alpha E_\nu], \quad (9)$$

where e^* is the Szegeti charge²⁰ and M is the reduced mass of the ion pair. In the brackets, α is the polarizability of the unit cell and αE_ν is the induced dipole in that cell from core polarization. These equations can be solved for the poles (transverse phonons) and zeros (longitudinal phonons) of the uniaxial dielectric function. The system becomes uniaxial because of the inequivalence of the dipole sums T_{zz} and T_{xx} . The form of the two tensor components $\varepsilon_{yy} = \varepsilon_{xx}$ and ε_{zz} of the dielectric function are given by¹⁷

$$\varepsilon_{jj}(\omega) = \varepsilon_{jj}(\infty) \frac{\omega^2 - \omega_{Lj}^2}{\omega^2 - \omega_{Tj}^2}, \quad j = x, z. \quad (10)$$

One can solve Eqs. (8) and (9) for various cases. For the bulk crystal, the LO and TO phonons are found by setting $\varepsilon_{yy} = \varepsilon_{xx} = \varepsilon_{zz} = \varepsilon_z(\infty)$, and we use the limit Eq. (3),

$$\omega_{LO}^2 = \omega_0^2 + \omega_p^2 \frac{2(\varepsilon_z(\infty) + 2)}{9\varepsilon_z(\infty)}, \quad (11)$$

$$\omega_{TO}^2 = \omega_0^2 - \omega_p^2 \frac{(\varepsilon_z(\infty) + 2)}{9}, \quad (12)$$

where

$$\varepsilon = 1 + \frac{4\pi\alpha/V_0}{1 - 4\pi\alpha/(3V_0)}$$

is the usual high frequency (real) Lorenz-Lorentz dielectric constant and

$$\omega_p^2 = \frac{4\pi e^{*2}}{MV_0}$$

is the ion plasma frequency. For optical phonons in a nanowire, the dipole sums T_{zz} and T_{xx} are given above. In this case, the pole and zero of $\varepsilon_{zz}(\omega)$ are the same as in the bulk

TABLE I. The bulk LO and TO Raman modes of cubic polar semiconductors from Refs. [21 and 22], and the calculated mode frequencies ω_{Tz} , ω_{Lz} , ω_{Tx} , and ω_{Lx} for a nanowire as described in the text. The dielectric constant, $\epsilon_z(\infty)$ data is from Ref. 23.

Crystal	ω_{TO} (ω_{TZ})(cm^{-1})	ω_{LO} (ω_{LZ})(cm^{-1})	ϵ_z (∞)	ϵ_x (∞)	ω_{Tx} (cm^{-1})	ω_{Lx} (cm^{-1})
GaAs	268.6	292	11.1	2.7	290.2	292.7
GaP	367	403	9.0	2.6	399.5	404.3
ZnS	274	349	5.1	2.3	337.9	353.6
SiC	796	972	6.5	2.5	950.5	980.6
ZnSe	206	252	5.9	2.4	245.9	254.4
ZnTe	179	206	7.3	2.5	202.9	207.2
CdTe	140	171	6.9	2.5	167.3	172.4
AlP	440	501	7.5	2.5	494.2	503.6
InP	303.7	345	9.5	2.6	341.3	346.4
InSb	179	200	15.7	2.8	198.8	200.4
AlSb	319	340	9.9	2.6	338.2	340.8

(i.e., $\omega_{Tz} = \omega_{TO}$; $\omega_{Lz} = \omega_{LO}$). For the other direction (xx or yy), the pole (ω_{Tx}) and zero (ω_{Lx}) are given by

$$\omega_{Tx}^2 = \omega_0^2 + \omega_p^2 \frac{(\epsilon_x(\infty) + 2)}{9(\epsilon_x(\infty) + 1)}, \quad (13)$$

$$\omega_{Lx}^2 = \omega_0^2 + \omega_p^2 \frac{7(\epsilon_x(\infty) + 2)}{9(3\epsilon_x(\infty) - 1)}, \quad (14)$$

where

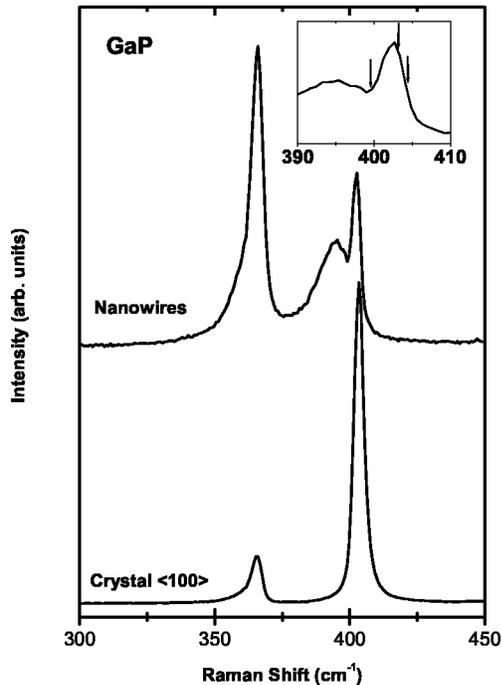


FIG. 1. Experimental Raman spectra from bulk crystalline GaP and GaP nanowires. The inset shows the nanowire spectrum on an expanded scale. The arrows in the inset indicate the calculated mode frequencies.

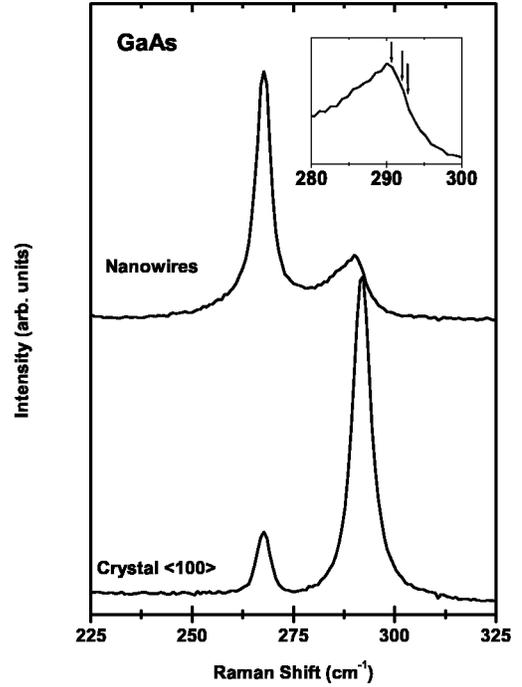


FIG. 2. Experimental Raman spectra from bulk crystalline GaAs and GaAs nanowires. The inset shows the GaAs nanowire spectrum on an enlarged scale. The vertical arrows in the inset indicate the calculated mode frequencies.

$$\epsilon_x(\infty) = \frac{3\epsilon_z(\infty) - 1}{\epsilon_z(\infty) + 1}.$$

In Table I we collect numerical results for a collection of polar semiconductors that show how the shape effect splits the phonons at $q=0$.

We next discuss the experimental Raman spectra at room temperature taken on thin films of GaP and GaAs nanowires. GaP and GaAs nanowires were prepared by the pulsed laser vaporization of a target containing the stoichiometric semiconductor compound mixed with 5 mol % of gold.^{24,25} The details of our sample preparation and characterization have been published elsewhere.²⁶ Raman spectra were collected with a JY-Horiba T64000 micro-Raman spectrometer in a backscattering configuration at room temperature in air using a $100\times$ objective on an Olympus BX40 confocal microscope.

Both GaP and GaAs crystallize in a zinc blende structure and the space group of the cubic unit cell is $F43m(T_d^2)$ containing four formula units. However, the primitive unit cell contains only one formula per unit cell and hence, there are three optical branches to the phonon dispersion curves. As there is no center of inversion in the unit cell, the zone center longitudinal optic (LO) and transverse (TO) optic modes are Raman active. In bulk GaP, at room temperature the TO mode frequency is at 367 cm^{-1} while the LO mode is observed at 403 cm^{-1} .²¹ In GaAs the TO and LO modes are at 268.6 and 292 cm^{-1} , respectively.²¹

In Figs. 1 and 2 we compare the Raman spectra of bulk and nanowire GaP and GaAs, respectively. The spectra were collected using 514.5-nm excitation. For both compounds we

see very little change in the low frequency Raman line between the bulk and the nanowire. This is testimony to the crystalline quality in the nanowire, and is consistent with the identification $\omega_{TO} \rightarrow \omega_{Tz}$. However, the high frequency Raman line of the nanowire is observed to downshift and asymmetrically broaden to a lower frequency relative to that in the bulk. The majority of this broadening is due to an unresolved surface phonon. This was deduced by observing the change in the position of this shoulder with the refractive index of a liquid in contact with the wires.²⁷ The peak position of the high frequency Raman line in the nanowire downshifts relative to the LO phonon in the bulk by 1 cm^{-1} in GaP and by 2 cm^{-1} in the case of GaAs. In the nanowire spectra, we cannot resolve the members of the high frequency triplet (ω_{Tx} , ω_{Lx} , ω_{Lz}) we predict here (the frequencies are listed in Table I). These modes are predicted to be split by $\sim 2 \text{ cm}^{-1}$. If we presume that the most intense member of the triplet is the ω_{Lz} mode, then the splitting between the two experimental nanowire peaks should be compared to ($\omega_{Lz} - \omega_{Tz}$). This splittings are 21.4 cm^{-1} (GaAs nanowire) and 34.5 cm^{-1} (GaP nanowire), which can be compared to ($\omega_{Lz} - \omega_{Tz}$) = 23.4 cm^{-1} (GaAs bulk) and ($\omega_{Lz} - \omega_{Tz}$) = 36 cm^{-1} (GaP bulk). Using the mean nanowire diameter ($d \sim 20 \text{ nm}$) determined from atomic force microscopy images

and the size-effect or phonon confinement model of Richter *et al.*,⁸ we calculate almost no change ($< 1 \text{ cm}^{-1}$) in the peak position or width of the nanowire lines. However, the downshift in the higher frequency peak position we observe in these nanowires is in good agreement with the shape effect

predictions. As a word of caution, it is important to point out here that in earlier experiments on bulk GaP doped with sulphur or tellurium by Galtier and Martinez,²⁸ it was found that only the LO mode downshifts by $\sim 1 \text{ cm}^{-1}$. However, in such cases a new bound phonon mode is also observed which is not observable in our case or is overshadowed by the surface phonon mode. We note that the LO phonon dispersion for bulk GaP is significantly weaker (by a factor of 3) than that of bulk GaAs. So, if the phonon dispersion was important for the observed peak shift, one would expect very different LO mode downshifts for GaP and GaAs, which is not observed.

In conclusion, we have presented theoretical and experimental evidence indicating that the two optic phonon modes in bulk cubic polar semiconductors split due to the long range dipolar interactions and the shape (wire geometry) of the sample. Our theory results in simple analytical expressions for the frequency of the longitudinal and transverse modes in the uniaxial wire (Table I). For small diameter polar nanowires, we expect to observe both a “size” effect and a “shape” effect in the Raman spectrum. Raman scattering therefore shows considerable promise as a fundamental and sensitive probe of nanowire phonons and should therefore be a valuable tool for nanowire device development.

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