Raman scattering of light in small crystals

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Raman scattering of light in small crystals is discussed. An analytical formula taking into
account dimensional quantization of phonon spectrum is derived to describe Raman spectra of
small crystalline particles. The calculations by this formula and previously known theory
have been compared to experimental data on Raman scattering in germanium and diamond.
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1. INTRODUCTION

In recent years, researchers' attention has been focused
on low-dimensional systems, such as quantum wires (one-
dimensional) and quantum dots (zero-dimensional). The
progress in this field is supported by developments in mod-
ern technologies used to manufacture such structures, and the
research is stimulated by their interesting physical properties
due to the dimensional quantum effects. Progress has been
remarkable in both experimental and theoretical studies of
dimensional quantization of electronic states in silicon, as a
result, red luminescence was detected in porous silicon
samples.[1]

Raman scattering is an effecient tool for studying phase
transitions in materials, phonon spectra, and excited states of
low-dimensional systems. In order to interpret Raman spec-
tra of silicon microcrystals, Richter *et al.*[2] and Campbell
et al.[3] developed a theory of phonon confinement, which was
later used to describe Raman spectra of other materials, such
as gallium antimonide,[4] gallium arsenide,[5] and diamond.[6]

The theory[2,3] is based on an *a priori* function of coordi-
nates which accounts for the confinement of a phonon wave
function in a finite crystal. According to this theory, phonon
modes in small crystals are described by wave packets whose
envelopes are Fourier transforms of confinement functions.
The Raman spectrum in this case is obtained by integrating
the response function of the system multiplied by the enve-
lope function over a region in the K-space (within the Bril-
louin zone). Specifically, in the Richter model the envelope
has the form $\exp(-q^2L^2/4)$, where q is the phonon wave
vector and L is the crystal size. Irrespective of the envelope
function, the theory assumed that the lifetime of a phonon
mode (the parameter $1/\Gamma_0$ in Eq. (6) of Ref. 3) was the same
as in a bulk crystal. Campbell *et al.*[3] investigated confine-
ment functions of various shapes and compared calculated
parameters of Raman spectra with experimental data. Then
they selected a function which led to the best agreement with
experiments on silicon. The flaw of the theory[2,3] is that it
ignores interference of phonons reflected from boundaries of
a low-dimensional object.

We have attempted to take into account interference ef-
fects in small crystals whose dimensions are comparable to
the lattice constant. In view of this, we have compared our
calculations with experimental spectra of materials having
the diamond lattice, both reported in literature and measured
by our group.

2. THEORY OF PHONON SPECTRA OF SMALL CRYSTALS

Calculations of phonon spectra of real crystals based on
exact solutions of the dynamic problem are usually imprac-
ticable because the number of degrees of freedom in a crystal
lattice is enormous. Therefore, various simplified (idealized)
models of crystals are of great importance. Let us consider
the phonon spectrum of a one-dimensional monoatomic
chain with additional bonds,[7] i.e., an atomic chain whose
components are acted upon by forces due to their neighbors
and also by an additional force (unlike the common chain
model), which arises when a particle is displaced from its
equilibrium position (Fig. 1). If the interaction with close
neighbors is only taken into account, motion equations of
atoms in such a chain are as follows:

$$m\ddot{U}(l,t) = -\gamma_0 U(l,t) + \gamma_1 [U(l-1,t) + U(l+1,t)$$
$$-2U(l,t)], \tag{1}$$

where $U(l,t)$ is the lth atom displacement from its equilib-
rium position $(l = 0,1,2, \ldots ,N)$, γ_0 and γ_1 are eleastic
constants, and m is the atom mass. In the equation of motion
for a usual atomic chain, the constant γ_0 is zero, unlike Eq.
(1). The frequency spectrum of the chain of N atoms with
additional bonds and periodic boundary conditions is de-
scribed by the following equations:

$$\Omega^2 = 4\frac{s^2}{a^2}\sin^2\left(\frac{qa}{2}\right), \tag{2}$$

$$\Omega_+^2 = \Omega_0^2 + 4\frac{s^2}{a^2}\sin^2\left(\frac{qa}{2}\right). \tag{3}$$

Here we have introduced the notations $s^2 = a^2\gamma_1/m$ and
$\Omega_0^2 = \gamma_0/m$, and

$$q = \pi n/L \tag{4}$$

is the phonon wave vector, a is the lattice constant, and
$L = Na$ is the chain length. The parameter n runs from zero
to $N-1$.

We will only discuss the optical phonon branch, which
determines Raman spectra of solids. The model phonon
spectrum derived from our theory allows us to describe gen-
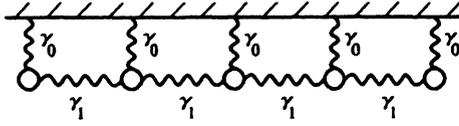eral properties of some branches of phonon spectra in com-

FIG. 1. One-dimentional monoatomic chain with additional bonds: circles show atoms and wiggly lines show elastic bonds; γ_0, γ_1 are coefficients of elastic bonds.

plex crystal lattices. In particular, Eq. (3) desribes the spectrum of vibrational excitons in NH_4Cl and $NaNO_3$. The case $\gamma_1 < 0$ corresponds to optical phonon spectra of crystals with the diamond lattice, when the following relation holds:

$$\Omega_+^2 = \Omega_0^2 - 4\frac{s^2}{a^2}\sin^2\left(\frac{qa}{2}\right). \tag{5}$$

Given the phonon spectrum, we can determine the phonon group velocity and mass:[7]

$$v = \frac{d\Omega_+}{dq} = \frac{s^2\sin(qa)}{a\sqrt{\Omega_0^2 - 4(s^2/a^2)\sin^2(qa/2)}}, \tag{6}$$

$$m = \frac{\hbar}{d^2\Omega_+/dq^2}$$

$$= \frac{\hbar[\Omega_0^2 - 4(s^2/a^2)\sin^2(qa/2)]^{3/2}}{s^2[\Omega_0^2 - 4(s^2/a^2)\sin^2(qa/2)]\cos(qa) + s^4\sin^2(qa)}. \tag{7}$$

In the continuous-medium approximation ($a \to 0$), Eq. (1) transforms to the following equation:

$$U''(x,t) - \frac{1}{s^2}\ddot{U}(x,t) - \frac{\Omega_0^2}{s^2}U(x,t) = 0. \tag{8}$$

The phonon dispersion relation (4) is transformed in this case to

$$E^2 = E_0^2 - s^2 p^2, \tag{9}$$

where $E = \hbar\Omega$, $E_0 = \hbar\Omega_0$, and $p = \hbar q$.

In the case of small q (slow phonons), Eq. (9) yields the conventional relation between energy and momentum:

$$E = E_0 - \frac{p^2}{2m_0}, \tag{10}$$

where m_0 is the phonon mass derived from Eq. (7) at $q = 0$.

The spectrum of oscillations of the atomic chain described by Eqs. (5), (9), (10) and characterized by the set of wave vectors defined by Eq. (4) is similar to that of a quasiparticle in a potential well with infinitely high walls. Really, when a particle is placed in a potential well, its spectrum is modified and becomes discrete.[8] For example, the solution of the continuous equation (8) in a potential well with a width L is the following:

$$U_n(x,t) = A\exp[i(q_n x - \Omega_n t)], \tag{11}$$

$$\Omega_n^2 = \Omega_0^2 - s^2 q_n^2, \tag{12}$$

$$q_n = \pi n/L, \quad n = 1,\ldots,L/a. \tag{13}$$

In this case, the quantization of the continuous spectrum is just the same as in the atomic chain, where the quantization is due to the finite number of atoms [Eq. (4)].

Given this similarity, we can use a model in which the phonon motion in a small crystal is described as particle motion in a potential well. This model is equivalent to the full reflection of a phonon from the crystal boundary. In fact, the transmission factor across an interface for an elastic wave is approximately equal to the ratio of sound velocities in the contiguous media.[9] In the case of an interface between diamond and air, $T \approx 10^{-2}$. Assuming this model, we select, in effect, only those solutions which correspond to phonon modes of a bulk crystal and do not take into consideration surface acoustic modes, which can be correctly accounted for only if real boundary conditions are known.

Under similar conditions of dimensional quantization, the number of phonon modes in a certain range of energy is different for the three phonon spectra described by Eqs. (5), (9), and (10).

Figure 2 shows energies of phonon modes calculated for one-dimensional quantum wells and shapes of the TO-phonon branch in diamond discussed above. The phonon wave vector is directed along the [100] axis, and the widths of quantum wells are $L = 5,7,10$ lattice constants.

3. GREEN'S FUNCTION OF THE PHONON EQUATION; RAMAN SPECTRUM OF A SMALL CRYSTAL

The phonon equation for a three-dimensional lattice with additional bonds, taking into account only interaction between neighbors, can be written as follows (we assume $\gamma_1 < 1$):[7]
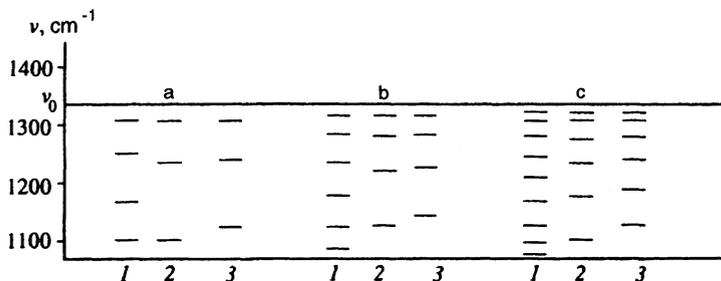

FIG. 2. Energies of diamond TO-phonon modes in the [100] direction in a quantum well with dimensions (a) $L = 5a$; (b) $L = 7a$; (c) $L = 10a$ (a is the lattice constant); 1) dispersion relation for the atomic chain with additional bonds [Eq. (5)]; 2) continuous approximation [Eq. (9)]; 3) slow-phonon approximation [Eq. (10)]; $\nu_0 = 1332$ cm^{-1} is the highest TO-phonon frequency.

$$m\ddot{U}(\mathbf{l}) = -\gamma_0 U(\mathbf{l}) + \gamma_1 \sum_{\alpha=1}^{3} \Delta_\alpha^2 U(\mathbf{l}), \tag{14}$$

$$\Delta_\alpha^2 U(\mathbf{l}) = U(\mathbf{l} - \mathbf{a}_\alpha) + U(\mathbf{l} + \mathbf{a}_\alpha) - 2U(\mathbf{l}). \tag{15}$$

As in the one-dimensional case, a solution of Eq. (14) in the form of monochromatic plane waves like that described by Eq. (11) yields an optical phonon spectrum in a crystal with dimensions $L_1 \times L_2 \times L_3$:

$$\Omega_+^2(\mathbf{q}_n) = \Omega_0^2 - \frac{s^2}{a^2}\left(\sin^2 \frac{\mathbf{q}_n \cdot \mathbf{a}_1}{2} \right.$$

$$\left. + \sin^2 \frac{\mathbf{q}_n \cdot \mathbf{a}_2}{2} + \sin^2 \frac{\mathbf{q}_n \cdot \mathbf{a}_3}{2} \right). \tag{16}$$

We assume that the crystal is cubic. Then

$$\mathbf{q}_n = \left(\frac{\pi n_1}{L}, \frac{\pi n_2}{L}, \frac{\pi n_3}{L} \right).$$

The Green's function of the lattice may be defined as a solution of the following nonuniform equation:

$$\sum_{\alpha=1}^{3} \Delta_\alpha^2 G(\mathbf{l},t) + \frac{1}{s^2}\ddot{G}(\mathbf{l},t) + \frac{\Omega_0^2}{s^2}G(\mathbf{l},t) - \frac{\Gamma_0}{s^2}\dot{G}(\mathbf{l},t)$$

$$= -\frac{1}{s^2}\delta(t)\delta(\mathbf{l}), \tag{17}$$

where $1/\Gamma_0$ represents the phonon lifetime. Let us seek the solution in the form of a Fourier series in the wave vectors of quantized phonons and a Fourier integral with respect to the frequency:

$$G(\mathbf{l},t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\Omega \frac{1}{N} \sum_{\mathbf{q}_n} G(\Omega,\mathbf{q}_n)\exp[i(\mathbf{q}_n \cdot \mathbf{l} - \Omega t)]. \tag{18}$$

Using the integral representation of delta-functions, i.e.,

$$\delta(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\Omega t}d\Omega, \quad \delta(\mathbf{l}) = \frac{1}{N}\sum_{\mathbf{q}_n} \exp(i\mathbf{q}_n\mathbf{l}), \tag{19}$$

and solving the resulting algebraic equation, we obtain the desired coefficients of the Green's function expansion:

$$G(\Omega,\mathbf{q}_n) = \frac{1}{\Omega^2 - \Omega_+^2(\mathbf{q}_n) - i\Omega\Gamma_0}, \tag{20}$$

where $\Omega_+^2(\mathbf{q}_n)$ is defined by Eq. (16).

The Raman spectrum of the crystal can be expressed as[10]

$$I(\Omega) = \sum_{\mathbf{q}_n} A\left| \left\langle \psi_S \frac{\partial\alpha}{\partial q} \psi_L \right\rangle \right|^2 \langle UU^* \rangle, \tag{21}$$

where $\langle \psi_S(\partial\alpha/\partial q)\psi_L \rangle$ is the matrix element of the derivative of the polarizability with respect to the normal coordinate, which determines the Raman spectrum, and $\psi_{L,S} = C \exp(i\eta_{L,S}\mathbf{r})$ are the wave functions of the incident and scattered photons. The correlation function of atomic oscillations versus frequency can be derived using the fluctuation–dissipation relation:
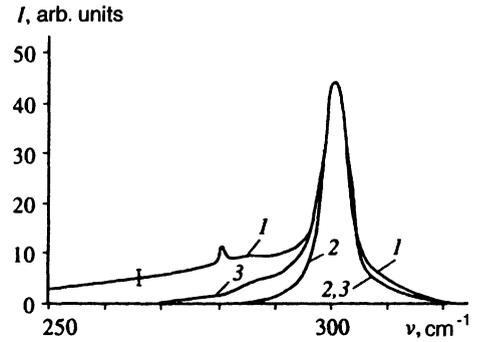

FIG. 3. Raman spectra of germanium microparticles: 1) experimental data for the s60 sample from Ref. 11; 2) calculation by the Richter model for 81 Å particles; 3) our calculation for 78 Å particles. The vertical bar shows the noise intensity in the experiment.

$$\langle UU^* \rangle = \frac{\hbar}{\pi}[n(\Omega) + 1]\,\text{Im}[G(\Omega,q)], \tag{22}$$

where $n(\Omega)$ is the occupation number.

Consider the following expression for the element of the polarizability derivative:

$$\left\langle \psi_S \frac{\partial\alpha}{\partial q} \psi_L \right\rangle = \left| \frac{\partial\alpha}{\partial q} \right| \int_V \exp\{i(\eta_L + \eta_S + \mathbf{q})\mathbf{r}\}dV. \tag{23}$$

In an infinite crystal $(V \to \infty)$ the volume integral yields a delta-function, which ensures conservation of energy and momentum. In the limit $|\eta_L|, |\eta_S| \ll |\mathbf{q}_1| = \pi/L$, integration over a limited volume yields

$$\int_{-L/2}^{L/2}\int_{-L/2}^{L/2}\int_{-L/2}^{L/2} \exp[i(q_x x + q_y y + q_z z)]dx\,dy\,dz$$

$$= 8\frac{\sin(q_x x)}{q_x}\frac{\sin(q_y y)}{q_y}\frac{\sin(q_z z)}{q_z}. \tag{24}$$

Thus Eq. (21) with matrix elements given by Eqs. (23) and (24) and the correlation function defined by Eq. (22) yields the desired Raman spectrum of a small crystal (a cube with the dimension L).

4. COMPARISON OF CALCULATIONS WITH EXPERIMENTAL DATA AND RICHTER MODEL

4.1. Germanium

Let us compare our calculations to the experimental data from Ref. 11 on germanium microparticles in a matrix of sodium chloride. Three samples with different average dimensions of particles were studied by Heath et al.[11] The Raman spectrum of the sample with the smallest particle size is shown in Fig. 3. According to the data obtained by transmission electron microscopy, the particle dimensions vary between 60 and 110 Å, while x-ray diffraction measurements yield the limits of 80 and 170 Å. The half-width of the Raman line is 2.50 cm^{-1}. The particle dimension estimated using the Richter model is 81 Å, which is in a good agreement with the measurements. The particle dimension derived using our model is 78 Å, which is also in agreement with independent experimental data. Figure 3 also shows spectra
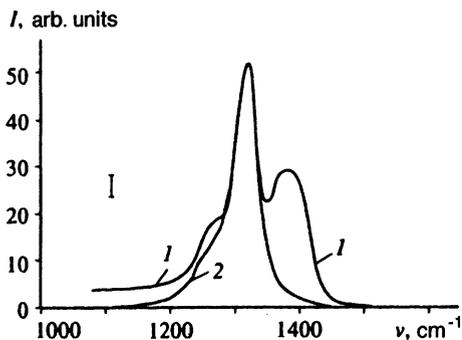
FIG. 4. Raman spectrum of ultrafine diamond particles: 1) experiment; 2) calculation for particles with a dimension $L = 40$ Å; $\Gamma_0 = 32$ cm^{-1}.

FIG. 5. Calculated spectrum of diamond particles with the dimension of 40 Å ($\Gamma_0 = 2$ cm^{-1}): 1) our model; 2) Richter model.

calculated using the two models. Heath et al.[11] assumed that the line half-width in a bulk crystal was 1.85 cm^{-1}. At frequencies below 295 cm^{-1}, both models yielded the scattered light intensity lower than in the experiment. This might result from the simplified form of the phonon spectrum (only one optical branch). Nonetheless, Fig. 3 indicates that our calculations adequately describe experimental data in the frequency range 285–295 cm^{-1}.

4.2. Diamond

Figure 4 shows the Raman spectrum of very fine diamond powder fabricated in an explosion. Guseva et al.[12] studied such powders using x-ray diffraction and electron microscopy. Previously we studied Raman spectra of several types of such powders.[6] Different techniques yielded particle dimensions ranging from 35 to 60 Å. In our latest experiments, the resolution of the Raman spectra was improved and the signal-to-noise ratio was increased by a factor of two (from 5:1 in Ref. 6 to 10:1). The spectral width of the monochromator slit in the experiment was 2.0 cm^{-1}. Diamond particles were implanted in a matrix of potassium bromide using the technique described in Ref. 6. The content of the diamond powder in the matrix material was about 1%. The spectra were recorded in the back-scattering configuration by a photon-counting system in a digital form. Since the signal intensity was very low, each spectrum was recorded thirty times, the measurements were averaged, and the resulting curves were smoothed.

Compared to the bulk diamond, the Raman spectrum of the powder is notably different. The intensity maximum of the fundamental mode is shifted from 1322 cm^{-1} in the bulk material by 6 cm^{-1} to the low-frequency side, and the line profile is apparently not a symmetrical Lorentzian curve. Its FWHM is 52 cm^{-1}. We interpreted the peak at 1380 cm^{-1} as oscillations of carbon groups on the particle surface due to bonds formed in the sp^2-hybridization of electronic orbitals.

Figure 5 shows spectra of diamond particles with dimensions of 40 Å calculated by the two models. In comparison with germanium, the dispersion of optical phonons in diamond is larger, so the Raman spectrum calculated by our model has a wider low-energy sideband and clear intensity oscillations in the range of 1250–1320 cm^{-1}. Calculations using Richter model do not yield such oscillations. The
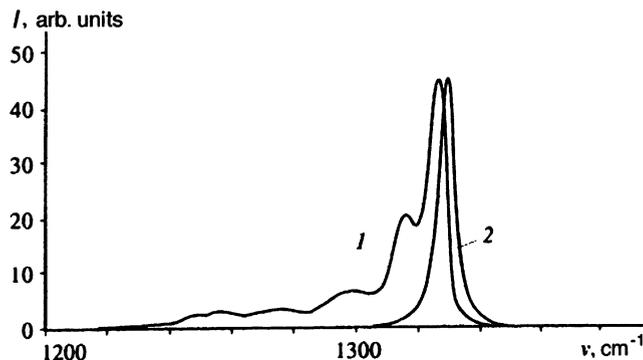
widths of calculated spectral lines in both cases are smaller than the experimental value. In the Richter model, this disagreement can be eliminated by taking a different shape of the phonon wave packet. In our previous work,[6] we used the envelope function $\exp(-q^2L^2/16\pi^2)$ proposed by Campbell and Fauchet.[3] As a result, the spectral width of the wave packet increased owing to the stronger phonon confinement inside the particle.

In our model, the disagreement between the calculated and measured line width can be eliminated by changing the phonon lifetime in comparison with the bulk crystal. This assumption is based on the chemical analysis of ultrafine diamond particles.[13] According to these data, the particles contain about 5 vol. % of various impurities, therefore the phonon lifetime may be shorter because of impurity scattering in the crystal lattice. Gubarevich et al.[13] measured the distribution of diamond particle dimensions by small-angle X-ray scattering. About 80% of particles have dimensions within 35–55 Å, and the distribution function peaks at about 40 Å. Taking this figure as a particle dimension, one can estimate the lifetime and correlation length of phonons in the particles. We have found a value of Γ_0 at which the calculated spectrum is the best approximation to the measured one. The calculation yields $\Gamma_0 = 32$ cm^{-1}, which corresponds to a phonon lifetime of $t = 1.04 \cdot 10^{-12}$ s (the respective spectrum is given in Fig. 4). According to our model, the phonons with the wave vector $q = \pi/L$ and the frequency $\Omega(\pi/L) = 1327.5$ cm^{-1} make the largest contribution to the Raman spectrum, and this parameter is in a good agreement with the experimental peak position. Equation (6) yields an estimate of the group velocity of these phonons: $v = 1.9 \cdot 10^5$ cm/s. Hence the correlation length for such phonons is $d = vt = 19.8$ Å, which equals about one half of the particle size.

5. CONCLUSION

We have investigated changes in phonon spectra of diamond crystals when their dimensions are reduced to several tens of angströms. The theoretical model of phonon spectra in such crystals is based on the motion of an optical phonon in a quantum well of a certain width with infinitely high

walls. We have established that the optical phonon spectrum of a nanocrystal consists of a set of levels different from that obtained by solving the traditional problem of a particle in a potential well with infinitely high walls.

We have obtained an analytical formula which describes distinctive features of Raman spectra of small crystals. In contrast to the results of the well-known Richter theory, we have obtained oscillations in the Raman spectrum due to dimensional quantization. Our results are confirmed by measurements of nanocrytals of germanium and diamond. Russian Editorial office.

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