

Raman Scattering from Acoustic Phonons Confined in Spherical Nanoparticles

R. KOSTIĆ*

Centre for Solid State Physics and New Materials, Institute of Physics

P.O. Box 68, Pregrevica 118, 11080 Belgrade, Serbia

Low-frequency Raman scattering from small spherical particles is analyzed. Frequencies of vibrational modes are calculated in elastic continuum approximation, which considers one nanoparticle as homogeneous elastic sphere. Parameters of this model are transverse (v_T) and longitudinal (v_L) sound velocities of material, i.e. elastic properties of bulk material. Frequencies of vibrational modes are scaled as function of mentioned bulk parameters for symmetric $l = 0$ and quadrupolar $l = 2$ spheroidal modes, in the case of stress-free boundary conditions. Calculated values are compared with the low-frequency Raman experimental results from literature (Ge, Si, CdS, CdSe, CeO₂, ...). These calculated relations can be practically used to examine nanoparticles of any bulk material. We presented also a procedure how to establish v_L and v_T of material from low-frequency Raman spectra and dimension d of particles.

PACS numbers: 61.46.Df, 63.22.-m

1. Introduction

The validity of elasticity theory in case of very small particles was the subject of continuous interest. Good agreement was found between results in valence-force-field model [1, 2], or atomistic approach [3] and the vibration frequencies of acoustic modes calculated using elasticity theory up to particle dimension of few nanometers.

The aim of this paper is to present some conclusions that follow from the basic case: a homogeneous spherical particle without surrounding medium in elastic continuum approximation.

2. Model and results

The vibrational theory of continuous elastic body is often used to describe a long-wavelength acoustic phonon that propagates in an ideal bulk crystal. Equation of motion parameters of the three-dimensional elastic body are mass density and elastic constants i.e. transverse v_T and longitudinal v_L sound velocities. As we attend to describe a confined acoustic phonon in a small crystal we must consider the boundary conditions at the surface of crystal, in our case sphere, and combine them with equation of motion in spherical coordinates [4–8].

Nanoparticles are often embedded in different material (matrix). Matrix can disable movement on the surface of nanoparticle. If there is no displacement at the particle surface, it is the case of so called rigid boundary conditions [6]. If properties of a matrix make it possible for

a nanoparticle to vibrate without restrictions we can assume that there is no force acting on the particle surface, i.e. radial components of the stress tensor at the surface are zero (it is the case of so-called free-surface boundary conditions) as applied in [6]. This condition is completely fulfilled if matrix is absent.

In this paper we present results of calculation for the stress-free boundary conditions. If we assume that particles are small spheres, equation of motion must be solved in spherical coordinate. It is useful to introduce dimensionless variables: $\eta = \frac{\omega R}{v_T} = \frac{\omega d}{2v_T}$ and $\xi = \frac{\omega R}{v_L} = \frac{\omega d}{2v_L}$, where R is radius of the particle (d is diameter).

In spherical case, each value of angular momentum quantum number l ($l = 0, 1, 2, \dots$) gives a series of solutions. We numerate these solutions n ($n = 0, 1, 2, \dots$). Eigen solutions are labeled as $\eta^{nl}(\xi^{nl})$, and eigenstates are labeled as (n, l) . Two types of vibrational modes are obtained: spheroidal and torsional modes. As $\omega^{nl} = 2\eta^{nl}v_T/d$ i.e. $\omega^{nl} = 2\xi^{nl}v_L/d$, each solution gives one linear dependence $\omega^{nl} = f(1/d)$.

According to the group theory analysis the spheroidal $l = 0$ and $l = 2$ modes are Raman active. Theory implies that the spheroidal mode $(0, 0)$ is the most intensive in the $l = 0$ series, and the most intensive of all Raman active modes. In a lot of low-frequency Raman scattering spectra only this mode was detected. The first quadrupolar mode is the most intensive in $l = 2$ series. The frequency of $(0, 2)$ mode is almost always lower than the $(0, 0)$ mode frequency.

We scaled $l = 0$ and $l = 2$ solutions as function of v_L/v_T . Results of these calculations are presented in Fig. 1.

* e-mail: rkostic@phy.bg.ac.yu

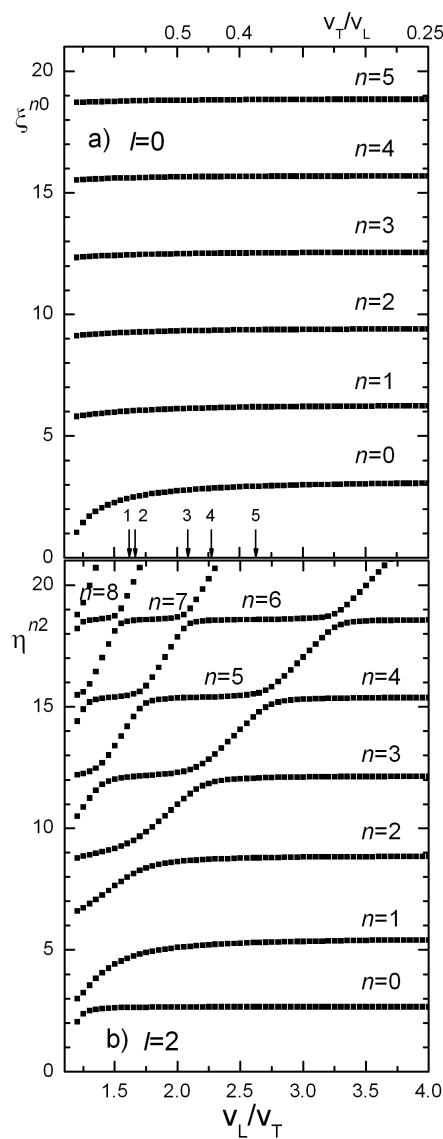


Fig. 1. Dimensionless eigensolutions: (a) ξ^{n0} as function of v_L/v_T for $l = 0$, $n = 0, 1, 2, \dots, 5$; (b) η^{n2} as function of v_L/v_T for $l = 2$, $n = 0, 1, 2, \dots, 8$. v_L/v_T values of Ge(1), Si(2), Ag(3), CdSe, CeO₂ and CdS(4) and Au(5) are assigned by arrows at the bottom of (a).

Sound velocity v_L is always bigger than v_T . We scaled v_L/v_T interval from 1.2 to 4. We present values of ξ^{n0} up to 20 i.e. $n = 5$, Fig. 1a. As we mentioned, intensity of Raman active modes decrease rapidly with increase of n and modes with higher n are not expected to be registered in experimental spectra. In case $v_L/v_T \gg 1$ eigensolutions converge to constant values.

In Fig. 1b we present values of η^{n2} up to 20. For $l = 2$ case η^{n2} eigensolutions are commonly presented to emphasize that displacements in the particle have both longitudinal and transversal nature.

If we have in mind relations $\omega^{nl} = 2\eta^{nl}v_T/d$ and $\omega^{nl} = 2\xi^{nl}v_L/d$, and calculated values presented in Fig. 1, we can establish any of relations $\frac{\omega^{n_1 l_1}}{\omega^{n_2 l_2}} = \frac{\xi^{n_1 l_1}}{\xi^{n_2 l_2}} \frac{v_L}{v_T} =$

$\frac{\xi^{n_1 l_1}}{\xi^{n_2 l_2}} = F\left(\frac{v_L}{v_T}\right)$. These ratios do not depend on particle dimension d , nor material parameters v_L or v_T directly. They do depend on v_L/v_T ratio, only.

As mode (0, 0) is the most intensive in Raman spectra, we will form relationships between frequency ω^{00} and frequencies from the series $l = 0, n = 0, 1, 2, \dots$ as $\frac{\omega^{n0}}{\omega^{00}} = \frac{\xi^{n0}}{\xi^{00}} = F_0\left(\frac{v_L}{v_T}\right)$. Results of these calculations are presented in Fig. 2a.

As we mentioned, ratios ω^{n0}/ω^{00} are independent of d . So, if we examine small spheres of material of known value v_L/v_T , characteristic ratio of frequencies ω^{10}/ω^{00} and ω^{20}/ω^{00} will be the same for all dimensions. This is one piece of information in attempt to interpret experimental spectra.

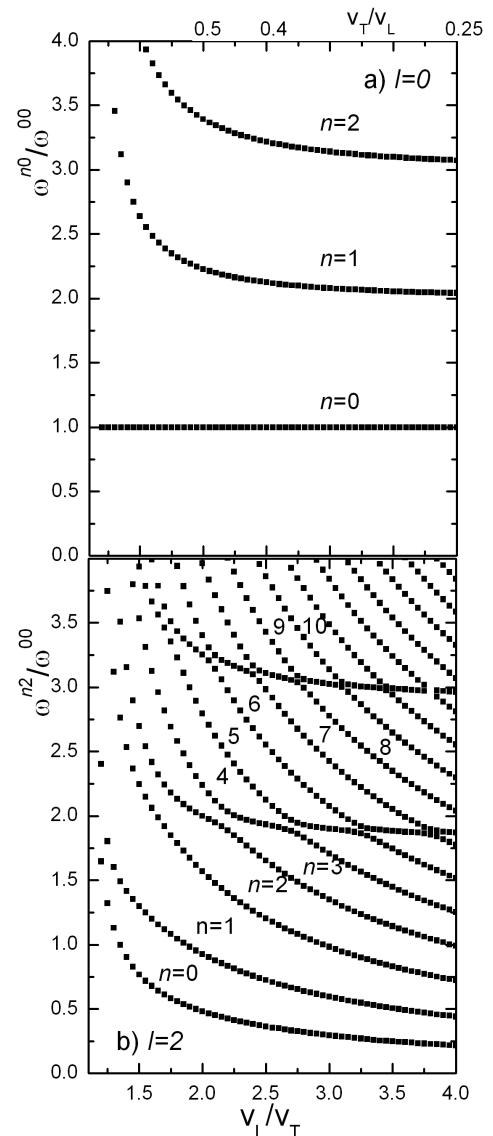


Fig. 2. (a) Frequency ω^{n0}/ω^{00} ratio as a function of v_L/v_T for $l = 0$, $n = 0, 1, 2$; (b) frequency ω^{n2}/ω^{00} ratio as a function of v_L/v_T for $l = 2$, $n = 0, 1, 2, \dots$

If v_L/v_T decreases below 2, ω^{10}/ω^{00} and ω^{20}/ω^{00} increase drastically. Similar behavior is found for $n > 2$ values that are not presented in Fig. 2a. In case $v_L/v_T > 2$, values of ω^{n0}/ω^{00} coverage to constant values become less informative about v_L/v_T value.

We also form relationships between frequency ω^{00} and frequencies from the series $l = 2, n = 0, 1, 2, \dots$, $\frac{\omega^{n2}}{\omega^{00}} = \frac{\xi^{n2}}{\xi^{00}} = F_2\left(\frac{v_L}{v_T}\right)$. Results of these calculations are presented in Fig. 2b.

All $l = 2$ solutions are rather sensitive to v_L/v_T value. Raman intensity of $l = 2$ modes is less than of $l = 0$ modes, and practically only first few modes from $l = 2$ series are expected to be registered and included in analysis. Mode (0, 2) is the most prominent one in $l = 2$ series. $\omega^{02} > \omega^{00}$ in a small region $v_L/v_T \leq 1.3$, $\omega^{02} \approx \omega^{00}$ at $v_L/v_T \approx 1.3$ and it is impossible to distinguish these two modes; $\omega^{02} < \omega^{00}$ in region $v_L/v_T > 1.3$ and ω^{02}/ω^{00} decreases with v_L/v_T increase. Parameters of the most materials are in $v_L/v_T > 1.3$ region. ω^{02} , as the strongest in $l = 2$ series, is often detected in experimental Raman spectra. As v_L/v_T increases, ω^{02} decreases and goes into the very low frequency region.

At the bottom of Fig. 1a v_L/v_T values of a few materials are assigned. Low-frequency Raman spectra for these, already studied, materials confirm results of this analysis.

Therefore, if one central feature in low-frequency Raman spectrum is registered it can be tentatively attributed to ω^{00} . Features below ω^{00} , if registered, are probably ω^{02} or ω^{12} frequency. Spectral features in spectral region over ω^{00} are probably ω^{10} (if $\omega_2 \approx 2\omega^{00}$) or some of the ω^{n2} modes from $l = 2$ series.

These results can be directly used if there are at least two features in low-frequency Raman spectra at frequencies ω_1 and ω_2 . It is reasonable to assume the most intensive Raman feature ω_1 to be ω^{00} . We must assume which mode from the $l = 0$ or $l = 2$ series corresponds to mode of ω_2 frequency. From ω_2/ω_1 value and curves from Fig. 2, v_L/v_T value can be determined. When v_L/v_T value is established, ξ^{00} value from $\xi^{00}(v_L/v_T)$ (Fig. 1a) can be determined. As we already know dimension d , we have assumed that $\omega^{00} = \omega_1$ and using relation $v_L = \omega^{00}d/2\xi^{00}$ values of v_L and v_T can be calculated.

Rest of features, if any, should be at the positions that correspond to calculated values v_L and v_T . These values have to be reasonable for the group of materials we are dealing with. If so, these v_L and v_T values can be adopted as new parameters of nanoparticle material. If not, we can try with some other assignment of ω_2 frequency, and follow the same procedure.

3. Conclusion

Dimensionless eigensolutions of Raman active vibrational modes of elastic sphere are scaled as function of bulk elastic parameters. We formulated rules that characteristic frequencies must obey. If there is more than one mode registered in low-frequency Raman spectra, calculated results give possibility to establish elastic parameters of the nanosphere material.

Acknowledgments

This work was supported by Serbian Ministry of Science and Technological Development, under project No. 141047 and OPSA-026283 project within the EC FP6 programme.

References

- [1] W. Cheng, S.F. Ren, P.Y. Yu, *Phys. Rev. B* **71**, 174305 (2005).
- [2] W. Cheng, S.F. Ren, *Phys. Rev. B* **68**, 193309 (2003).
- [3] N. Combe, J.R. Huntziger, A. Mlayah, *Phys. Rev. B* **76**, 205425 (2007).
- [4] L. Saviot, B. Champagnon, E. Duval, I.A. Kudriavtsev, I.E. Akimov, *J. Non-Cryst. Solids* **197**, 238 (1996).
- [5] E. Roca, C. Trallero-Giner, M. Cardona, *Phys. Rev. B* **49**, 13704 (1994).
- [6] L. Saviot, D.B. Murray, Maria del Carmen Marco de Lucas, *Phys. Rev. B* **69**, 113402 (2004).
- [7] L. Saviot, D.B. Murray, *Phys. Rev. B* **72**, 205433 (2005).
- [8] M. Montagna, *Phys. Rev. B* **77**, 045418 (2008).