Non-lineal equations for the Raman spectroscopy analysis

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Abstract. We study some equations used in the analysis of the materials of the Raman spectrum. Some equations are, phonon lifetime, related to the full width at half maximum (FWHM), the size of the nanoparticles, as explained with the equation of the intensity of Raman Spectrum; the Gruneisen parameter isothermal and isobaric explained by the frequency shift of the Raman scattered light; it is directly related to the structural properties of the material. The frequency shift may be dependent upon the application of temperature, hydrostatic pressure and the composition of the material itself. Furthermore, it is possible to obtain the behavior of anharmonic material using the Raman scattering frequency shift.

1. Introduction
Raman spectroscopy probing the molecular and crystal lattice vibrations and hence being bottom up approach of the matter appears as one of the most powerful techniques in the study of nanomaterials and nanostructures. \cite{1, 2, 3, 4, 5, 6, 7, 8}.

Previously we had assumed that the dipole moment of the molecule, $P$, in an electric field is:

$$P = \mu_0 + \alpha E$$  \hspace{1cm} (1)

where $\mu_0$ is the permanent dipole moment, $\alpha$ is the polarizability, and $E$ is the electric field of the light wave. However, when the intensity of the incident light is sufficiently large, the induced oscillation of the dipole moment becomes nonlinear:

$$P = \mu_0 + \alpha E + \beta E E + \gamma E E E$$  \hspace{1cm} (2)

The second-order nonlinear phenomena are described by the second term of the equation. One of the best known nonlinear optical phenomenon of the third-order is the stimulated Raman scattering.

The variation in both the Stokes and anti-Stokes component intensities with temperature for a particular experimental. These data are in very good agreement with quantum mechanical predictions for the intensities temperature variation given here as:

$$I_{st} \propto \frac{\hbar}{2 \omega_s} (\omega_l - \omega_s)^4 \left[ 1 + \left( e^{\frac{\hbar \omega_s}{kT}} - 1 \right)^{-1} \right]$$  \hspace{1cm} (3)
Here $\omega_s$, is the phonon frequency, $\omega_L$ is the line center frequency of the laser excitation source, $T$ is the sample temperature measured by optical, and $\hbar$ and $k$ are the Planck and Boltzmann constants. The proportionality constant in equations (3) and (4) include the variation in the polarization with normal coordinate separation and the collection efficiency of the optics, and are essentially equal for both the Stokes and anti-Stokes components. The close agreement between the measured and theoretical temperature dependence suggests that the sample is optically thin to the laser, Stokes, and anti-Stokes radiation [10].

The Stokes to anti-Stokes intensity ratio

$$\frac{I_{st}}{I_{a-st}} \propto \frac{\hbar}{2\omega_s} \left(\omega_L + \omega_s\right)^4 \left(e^{\frac{\omega_s}{RT}} - 1\right)^{-1}$$

(4)

The lifetime of phonons is an important physical quantity, since it reveals detailed information on the anharmonic phonon-phonon interactions in a solid. Even in a perfect crystal at low temperature, phonons have a finite lifetime due to the decay, through anharmonic interactions, into combinations of phonons of different energy. Selection of the excitation wavelength depends on several factors. The Raman differential scattering cross-section varies inversely with the fourth power of the excitation wavelength by the proportionality formula:

$$\sigma \propto \left(\tilde{\nu}_0 - \tilde{\nu}_{vib}\right)^4$$

(5)

where $\tilde{\nu}_0$ is the wavenumber of the incident radiation ($1/\lambda_0$) and $\tilde{\nu}_{vib}$ is the wavenumber of the vibrational mode ($\nu_{vib}/c$).

The photon lifetimes as a function of temperature can be accurately measured by Raman spectroscopy. However, the temperature dependent Raman scattering measurement can be used to estimate not only the temperature variation of the phonon lifetimes, but also the anharmonicity in the vibrational potential accurately. The finite values of the lifetimes are predominantly due to phonon-phonon interaction, which is highly temperature-dependent, but also has a contribution due to the scattering by crystal defects, and boundary scattering (phonon propagation is limited by the sample dimension) which is almost temperature-independent [9].

The anharmonicity present in the vibrational potential for the two modes is estimated by means of numerically calculating the anharmonic constants. Furthermore, the temperature-independent broadening due to the inherent disordered nature of the crystal and boundary scattering is also estimated for the two modes.

In the quasiharmonic model, phonon modes behave harmonically with lifetimes, but their frequencies are altered by the effects of volume on the interatomic potential. Pure anharmonicity originates with phonon-phonon interactions, which increase with temperature. Pure anharmonicity contributes to shifts in phonon frequencies, but also causes phonon damping and lifetime broadening of phonon peaks. To separate the peak shifts caused by pure anharmonicity from the shifts caused by quasiharmonicity, we treat the mode frequency $\omega_j = \omega_j(V,T)$ as a function of volume and temperature.

$$\left(\frac{\partial \ln \omega_j}{\partial T}\right)_P = -\frac{\beta}{\kappa} \left(\frac{\partial \ln \omega_j}{\partial P}\right)_T + \left(\frac{\partial \ln \omega_j}{\partial T}\right)_V$$

(7)
where \( j \) is the phonon mode index, \( \beta \) is the volume thermal expansivity, and \( \kappa \) is the isothermal compressibility. This is a general method to separate phonon quasiharmonicity from phonon anharmonicity and is not unique for rutile structures, for example. The left hand side gives the directly measurable temperature-dependent isobaric frequency shift, including both quasiharmonic and pure anharmonic behavior. The first term on the right-hand side, the isothermal frequency shift as a function of pressure, is the quasiharmonic contribution, which is also measurable. By defining a mode Grüneisen parameter as the proportionality of the relative change of the mode frequency to the relative change of volume, \( \gamma_j = \frac{\partial \ln \omega_j}{\partial \ln V} \). The second term on the right-hand side of Eq. (7) is the frequency shift from the pure anharmonicity, which depends on temperature and not volume. From the difference between the isobaric and the isothermal frequency shifts, the pure anharmonicity can be determined experimentally [11].

2. Experimental
Raman scattering measurements were performed using a Jobin-Yvon T64000 triple monochromator with a CCD detector. The exciting light from an argon laser was focused on the samples with an optical microscope using a long working distance 50X objective. For the low temperature measurements, in the 10 K to 300 K range, a helium closed cycle cryostat was used while for high temperature, in the 300 K to 850 K range, an optical micro furnace was used. The frequency values of each vibrational mode were obtained by fitting asymmetric Lorentzian line shapes.
3. Results and Discussion

The observed softening of the mode E1, shown in Fig. 1. These temperature dependent changes can be attributed to the anharmonicity in the vibrational potential, which leads to the decay of optical phonons into low-energy phonons. Furthermore, the inherent disorder in the crystal provides decay channels and leads to broadening of the phonon. This term is almost temperature independent. The FWHM of Raman lines, the inverse of the phonon lifetime, has been measured repeatedly in the past in particular for diamond-type crystals. The main attention was focussed on the temperature dependence [3], and on the dependence on isotopic composition [3, 4]. While the temperature dependence of the FWHM is governed mainly by the change in the phonon occupation numbers, its pressure dependence originates only from the pressure induced changes in the phonon dispersion relation and from the change of the anharmonic force constants. The pressure-induced change in the linewidths is a comparably small effect. Therefore, special precautions have to be taken to determine the correct FWHM of the phonon modes. The finite resolution of the spectrometer has to be taken into account. The experimental lineshape is usually a convolution of a Lorentzian-type phonon with the Gaussian spectrometer profile. The resulting lineshape is the so-called Voigt lineshape. To determine the spectrometer profile, the spectrum of a nearby the line was measured for each Raman spectrum [12].

The variation in the fullwidth at half maximum intensity (FWHM) with temperature is shown in Fig.2. The temperature-dependent Raman scattering indicates that the decrease in the phonon lifetime with increasing temperature is predominantly due to the decay of strongly interacting optical phonons into weakly interacting low-energy phonons. A contribution for the phonon lifetime also comes from the scattering by inherent crystal defects and from the boundary scattering, but this contribution is found to be temperature-independent.

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