Birefringence effect in Raman scattering of anisotropic materials

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Abstract
We added birefringence and interference consideration to the conventional classical Raman scattering theory commonly found in literature to address birefringence and interference effect in Raman spectroscopy. We hope the new result can be useful for ab initio calculations as well as experimental studies.

Introduction
Most Raman spectra ab initio studies cite the two books by P. Brüesch and M. Cardona for the equations to calculate Raman intensities. [1,2] However, the cited equation could not account for birefringence and interference effect, which arise from anisotropy and finite thickness of the sample. Here, we redevelop the classical Raman scattering theory to address these shortcomings.

Layered materials are often anisotropic and few-layer thin, where birefringence and interference can have serious impact. There are efforts to add birefringence correction to angle resolved polarized Raman spectroscopy of 2D materials in literature. [3,4] But their equations are of empirical nature, with corresponding parameter fitted from experimental results. In comparison ours can be used in ab initio calculations and offers clearer physical picture. And crucially our conclusions differ, the key difference being that they approximate Raman active phonon wave vectors to 0 while we don’t.

Theory
When light propagates through a birefringent material, it will split into two mutually orthogonal polarized parts, each with different propagation speed. One is ordinary ray and the other is extraordinary ray. Actually, in biaxial birefringence both are extraordinary rays. But we can still denote them as o ray and e ray for convenience.

According to classical electrodynamics, the electric field of an incident light \( \vec{E} \) will induce a dipole moment \( \vec{M} \) in an atom.

\[
\vec{M} = \varepsilon_0 \vec{x} \vec{E}
\]

Where \( \varepsilon_0 \) is vacuum permittivity. \( \vec{x} \) is polarizability tensor.

For the k-th atom in the f-th unit cell of the crystal, the dipole moment becomes

\[
\vec{M}_{fk} \propto \vec{x}_{fk} \vec{E}_{al} e^{i(\omega t - n_{al} \vec{k}_e \vec{r}_{fk})}
\]

Where \( \vec{E}_{al} \) means the electric field of incident light l polarized in direction a, which must
be in one of the polarization directions of o ray or e ray in birefringent materials. And \( n_{al}, \omega_l, \vec{k}_l \) means the corresponding refractive index, frequency and vacuum wave vector, respectively. \( \vec{r}_{fk} \) is the coordinate of \( f_k \)-th atom. Although the electric field is written in complex form we actually only take the real part of it. Thus, the polarizability tensor must be real.

The polarizability tensor can be written in two parts.

\[
\vec{x}_{fk} = \vec{x}_{k}^0 + \vec{x}_{fk}^p
\]

The first part \( \vec{x}_{k}^0 \) is independent of time and position of unit cell. It is responsible for Rayleigh scattering. The second part is the polarizability induced by atom movement

\[
\vec{x}_{fk}^p = \frac{\partial \vec{x}_{k}}{\partial \vec{r}_k} \cdot \vec{u}_{fk} \propto \frac{\partial \vec{x}_{k}}{\partial \vec{r}_k} \cdot \left( \vec{g}_k(q,i) \frac{e^{i(\omega(q,i)t-\vec{q} \cdot \vec{r}_{fk})}}{\sqrt{m_k}} \pm c. c. \right)
\]

where \( \vec{u}_{fk} \) is displacement of atom. \( \vec{g}(q,i) \) is the eigen vector of a particular vibration mode with wave vector \( q \) and frequency \( \omega(q,i) \). \( m_k \) is the atomic mass.

This part is responsible for Raman scattering. Now, according to classical radiation theory an oscillating dipole with frequency \( \omega \) will emit energy per unit solid angle at a rate of [1,2]

\[
\frac{dW}{d\Omega} = \frac{\omega^4}{16\pi^2\varepsilon_0 c^3} |\vec{e} \cdot \vec{M}|^2
\]

Hence, each atom will emit a scattered light of

\[
\vec{E}_{fk}^b \propto \vec{M}_{fk}^b e^{i(n_{bs}k_s \cdot \hat{r}_{fk})} e^{i(\omega(q,i)t-\vec{q} \cdot \vec{r}_{fk})} \pm c. c.
\]

where annotation \( s \) denotes scattered light, \( b \) denotes polarization or oscillation direction, which must be in one of the o ray or e ray polarization directions of the scattered light.

The total Raman scattered light by a particular vibration mode will be all these individual scattered lights added up

\[
\vec{E}_s \propto \sum_{j=0}^{\infty} \vec{E}_{al}^b \left( \vec{E}_{bf}^b \cdot \frac{\partial \vec{x}_{k}}{\partial \vec{r}_d} \right) e^{i(\omega_{al}t+(n_{bs}k_s-n_{al}k_l)\vec{r}_{fk})} A \left( \frac{g_{kd}(q,i)}{\sqrt{m_k}} - e^{i(\omega(q,i)t-\vec{q} \cdot \vec{r}_{fk})} \right) \pm c. c.
\]

where annotation \( d \) means axis direction. \( \vec{E}_{bf}^b \) is unit vector at \( b \) polarization direction. \( A \) is a complex number representing phase and magnitude of vibration of the phonon.

It can be seen that \( q \) should satisfy

\[
\pm q = Re(n_{al})k_l - Re(n_{bs})k_s
\]

\[
\pm \omega(q,i) = \omega_l - \omega_s
\]

Otherwise scattered lights from different atoms will annihilate each other. This relationship corresponds to conservation of energy and momentum in quantum picture, with the + sign corresponding to creation of a phonon and is called stokes process, while
the - sign corresponds to anti-stokes process.

It seems from above derivation that the stokes process and anti-stokes process have nearly the same intensity. Unfortunately, this is wrong. The correct intensity from quantum theory would be \[ I \propto \frac{\omega_s^4}{\omega(q,j)} \left( \frac{\bar{n} + 1}{\bar{n}} \right) \]

where \(\bar{n}\) is the mean occupation number of the particular phonon and it follows Bose–Einstein distribution. Generally, at room temperature the phonon occupation number is close to zero so experiments usually measure stokes process only.

We can see that there is no simple rule regarding Raman intensities. It is a complicated interplay between refractive index, phonon wave vector and sample size. Normally the incident light wave length is much larger than the size of primitive cell of the crystal, as a result the Raman active phonon wave vector is also very close to the center of Brillouin zone, or the Gamma point. In presence of birefringence the Raman scattered light will split into multiple polarized parts, each one is incoherent to each other because they come from scattering with different phonons. But their frequency difference may not be discernible because the derivatives of phonon frequency at Gamma point is 0 due to \(\omega(q)\) being an even function. This effect can be most likely observed with angle resolved polarized Raman spectroscopy. In materials with limited sizes the phonon wave vector will no longer be continuous in the Brillouin zone, thus we may observe that the Raman intensity vary erratically with different laser light frequencies.

**Discussion**

In this section we compare with experimental results from literature to give a qualitative verification to our theory.

The theory predicts that the scattered Raman light can have different frequencies at the different polarization directions in birefringent material. This indeed is the case in the polarized Raman spectroscopy of black phosphorus in the figure below. [5] The frequency difference between zigzag and armchair polarization direction is consistent across different temperatures. And the difference is also small compared with full-width-at-half-maxima of the Raman spectral lines. Actually, the most prominent feature in the below figure is temperature dependence of Raman frequencies. This is due to anharmonicity effect. The half-maxima width is also be attributable to this effect.
We also predict that the different polarizing parts of Raman scattered light in birefringence can be incoherent to each other. This can be best manifested in the angle resolved polarized Raman spectroscopy profile. In the common backscattering configuration of Raman spectroscopy, the x, y axis can be made to coincide with the polarization directions of o, e ray. If the Raman tensor is of the form

\[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & *
\end{pmatrix}
\]

angle resolved polarized Raman intensity profile with the polarization direction of scattered light parallel to that of incident light in isotropic material will be \( I_\parallel(\theta) \propto 1 \). But in birefringent case with incoherent assumption it will be \( I_\parallel(\theta) \propto \sin^4 \theta + \cos^4 \theta \).

However, it should be cautioned that if we assume instead the different polarizing parts to be out of phase rather than incoherent, which is the assumption made in the literature [3,4], we can also obtain the same profile. Thus, this theory does not offer an immediate benefit in terms of agreeing more with experiments. But it gives a clearer physical picture. It can also be used for ab initio calculations. The literature also did not try to calculate the phase but rather treat it as an empirical parameter.

**Conclusion**

We successfully develop a detailed Raman scattering theory that can quantitively assess birefringence and interference effect in anisotropic material. It can be used in ab initio calculations. The theory gives different predictions and interpretations to the birefringence phenomena in Raman spectroscopy than the literatures we find. We hope this theory can help shed new light on the birefringence effect in Raman scattering for future theoretical and experimental studies.
Reference

[1] Light Scattering in Solids II, edited by M. Cardona, and G. Güntherodt (Springer-Verlag, Berlin, 1982).

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[3] Mao, N., Wu, J., Han, B., Lin, J., Tong, L. and Zhang, J. (2016), Birefringence-Directed Raman Selection Rules in 2D Black Phosphorus Crystals. Small, 12: 2627-2633. doi:10.1002/smll.201600295

[4] Kim, J., Lee, J., Lee, J., Park, H. J., Lee, Z., Lee, C., & Cheong, H. (2015). Anomalous polarization dependence of Raman scattering and crystallographic orientation of black phosphorus. Nanoscale, 7(44), 18708-18715.

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