PHOTONICS Research

Elucidation of "phase difference" in Raman tensor formalism

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The so-called "phase difference" is commonly introduced as a phenomenological parameter in Raman tensor theory, so as to fit the experimental data well. Although phase difference is widely recognized as an intrinsic property of crystals, its physics still remains ambiguous. Recently, Kranert *et al.* have presented a new formalism to explain the origin of phase difference theoretically. Here, we systematically conducted experimental research with polar phonons in wurtzite crystals, the results of which strongly suggest that the phase difference should be predetermined in a Raman tensor, rather than be treated as Raman tensor elements traditionally or as an intrinsic property. On the grounds of pinpointing existing logical flaws in Raman tensor study, we provide a logically clear paradigm.   © 2018 Chinese Laser Press

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1. INTRODUCTION

Raman characterization is widely applied in materials study since it can powerfully reveal the internal vibration modes (phonons). In Raman scattering experiments, the Raman tensor is derived from the angle-dependent polarized Raman spectra and contains various information, for example, the vibration symmetries, polarities, and anisotropies of crystals [1–3]. In the widely adopted Raman tensor formalism established half of a century ago, there is a phenomenological parameter noted as "phase difference," which has to be introduced to make the theory fit experiments well [4–12]. However, the lack of clear understanding of the physical meaning of phase difference has become the theory's Achilles heel. Recently, Kranert *et al.* have provided new insights and explained the origin of phase difference through an *ab initio* method [13,14], but their experimental support seems inadequate. We acknowledge their viewpoint and systematically conduct experimental research aiming at phase-difference-related polar phonons in four typical wurtzite compounds, namely, AlN, GaN, ZnO, and SiC. Based on their theory, we further elucidate the physics of phase difference.

According to group theory, the polar phonon in binary wurtzite compounds possesses an A_1 symmetry [15] and vibrates along c axis; it thus induces a deviation of the negative and positive charge centers, giving rise to its polarity. The A_1 phonon is Raman-active, and its Raman scattering intensity is given as

$$I \sim |e_s \cdot R[A_1] \cdot e_i|^2, \tag{1}$$

where e_s and e_i denote the unit polarization vector of incident and scattered light, respectively. $R[A_1]$ is the defined Raman tensor of the A_1 phonon, which describes its scattering behaviors. Currently, the commonly used Raman tensor of the A_1 phonon is written as

$$R[A_1] = \begin{bmatrix} |a|e^{i\varphi_a} & & \\ & |a|e^{i\varphi_a} & \\ & & |b|e^{i\varphi_b} \end{bmatrix}, \tag{2}$$

where a and b are both real numbers, and φ_a and φ_b represent the phases of Raman tensor elements. Since the Raman intensity is determined by the square of the absolute value of the Raman tensor, we can multiply the Raman tensor by an absolute phase $e^{-i\varphi_a}$ and the scattering intensity still remains the same. Hence, the Raman tensor can be also written as

$$R[A_1] = \begin{bmatrix} |a| & & \\ & |a| & \\ & & |b|e^{i(\varphi_b-\varphi_a)} \end{bmatrix}. \tag{3}$$

For non-polar phonons (i.e., E_1), the phases of the Raman tensor elements have no influence on its scattering intensity because they share the same value. However, this is not the case when it comes to polar phonons. For the polar A_1 phonon in wurtzite crystals, calculating Eq. (1) for a light incident to the m plane in backscattering geometry under a parallel polarization configuration ($e_s//e_i$) gives the angle-dependent intensity as

$$I_{A_1}^{\parallel}(\theta) \sim |a|^2 \sin^4\theta + |b|^2 \cos^4\theta + \frac{1}{2}|a||b|\sin^2(2\theta)\cos\varphi_{a-b}, \tag{4}$$

where $\varphi_{a-b} = \varphi_a - \varphi_b$ is the so-called phase difference widely introduced in current Raman tensor studies.

Equation (4) shows that the phase difference in the polar A_1 phonon exerts significant influence on Raman scattering intensity. Hence, it is necessary to obtain the phase difference when studying Raman scattering of polar phonons. Although the results of calculation using Eq. (3) fit well with experiments, few theories have given a convincing explanation of the physical meaning and the origin of phase difference. In current studies, a widely applied method introduces phase difference to a Raman tensor, which takes the form of Eq. (2), and uses Eq. (3) to fit experimental data so as to obtain all elements (including phase difference) in Raman tensors [10,16]. This method indicates that phase difference, together with Raman tensor elements, is characterized as the intrinsic properties of crystals. Previous study has also rendered Raman tensor elements and phase difference as parameters characterizing crystalline anisotropy [6]. However, for a long time, no convincible theory was given to expound upon the physical meaning of phase difference, which significantly attenuates its physical clarity. In particular, the ambiguity of the physical meaning of the phenomenological parameter-phase difference is detrimental to our efforts in analyzing the properties of crystals using Raman tensors.

Recently, a new reasonable theory was presented by Kranert *et al.* [13]. They first pointed out that birefringence must be taken into consideration in the case of bulk crystals. Through the *ab initio* method, they suggested that a 2×2 Raman tensor of the A_1 phonon, in consideration of a light incident to the m plane of bulk wurtzite crystals, be expressed as

$$\begin{bmatrix} |a| & \\ & |b|e^{i\frac{\pi}{2}} \end{bmatrix}, \tag{5}$$

where a, b are real numbers. Obviously, the general 3×3 Raman tensor can be written as

$$\begin{bmatrix} |a| & & \\ & |a| & \\ & & |b|e^{i\frac{\pi}{2}} \end{bmatrix}. \tag{6}$$

The new theory indicates that the $\pi/2$ phase in Eq. (6) is caused by the birefringence in optical measurement of a Raman scattering experiment. After substituting Eq. (6) into Eq. (1), the new intensity-angle relationship is given as

$$I_{A_1}^{\parallel}(\theta) \sim |a|^2 \sin^4\theta + |b|^2 \cos^4\theta. \tag{7}$$

It is readily seen in Eqs. (6) and (7) that phenomenological parameters are absent, removing previous ambiguities in physics. Moreover, the comparison of the new Raman tensor [Eq. (6)] and the traditional one [Eq. (3)] leads to a surprising conclusion, that is, the phase difference of wurtzite bulk crystals in traditional theory should possess the same value. This implicates that the phase difference might not be regarded as an intrinsic property, as it varies within different crystals.

Now there is a chasm between traditional and new Raman tensors in phase difference indication. Regarding this, it is significant to prove the validity of the new theory through more

experiments. Hereby, we conducted Raman scattering experiments on several wurtzite crystals and analyzed their angle-dependent polarized Raman spectra. Our results strongly supported the new theory.

2. EXPERIMENTAL RESULTS AND DISCUSSION

Commercial AlN, GaN, ZnO, and 6H-SiC bulk single crystals were used as samples in our experiments. A Renishaw Raman spectrometer (inVia Reflex) was employed to conduct angle-dependent polarized Raman measurements, and a 532 nm laser was used for exciting light. The excited laser was concentrated on the m-plane surface of crystals. The geometric configuration of Raman scattering accords with the configuration $X(\alpha\alpha)\overline{X}$. Here, X is the propagating direction of incident light and $\overline{X}$ that of scattered light, and they both are along the x axis of the crystals. α denotes the polarization of excited and scattering light. Further, $\alpha = \mathbf{z} \cdot \cos\theta$, where θ is the angle between the z axis of the crystals and the polarization vector. The specific geometric configuration can be found in our previous work [4].

As shown in Fig. 1, the intensity-angle relationship of the A_1 phonons in each crystal was fitted using a traditional and a new Raman tensor, respectively. The fitting results and the original data were displayed in Fig. 2 and Table 1. It can be readily seen from Fig. 2 that both theories fit the experimental data well, and it can be further consolidated by the very similar anisotropic ratios acquired from different theories shown in Table 1. Most importantly, as shown in Fig. 3, the values of phase difference are unanimously confined to around $\pi/2$, while the anisotropic ratios display obvious differences in the four compounds. Considering this, it is reasonable to believe
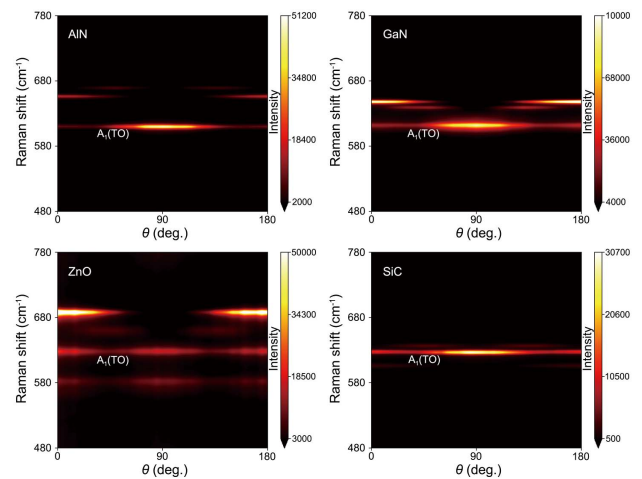

Fig. 1. Angle-dependent polarized Raman spectra of AlN, GaN, ZnO, SiC bulk single crystals obtained on the m plane under a parallel polarization configuration for different rotation angles increasing from $0°$ to $180°$ with a step of $5°$. The A_1(TO), E_1(TO), E_2^2 phonons of each sample can be clearly identified. The parallel polarization configuration is written as $X(\alpha\alpha)\overline{X}$ in shorthand, where X and $\overline{X}$ denote the direction of propagation of incident and scattered lights, respectively; α represents the direction of polarization. Here, $\alpha = \mathbf{z} \cdot \cos\theta$, in which θ is the angle between the polarization vector and the $\mathbf{z}$ axis.
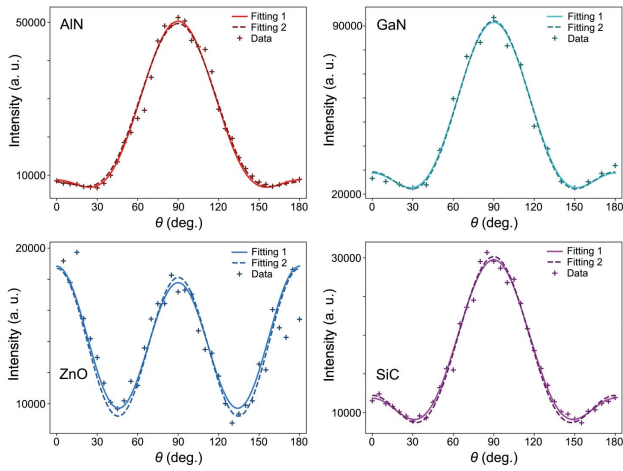
Fig. 2. Fitted A_1(TO) intensity-angle relationship of four wurtzite compounds using a traditional and a new Raman tensor, respectively. The "data" in the plot refers to the original experimental data, "Fitting 1" represents the fitting result using traditional theory, while "Fitting 2" represents the result of the new theory.

Table 1. Raman Tensor Elements of Four Wurtzite Compounds Fitted from Angle-Dependent Polarized Raman Spectra Using Traditional and New Raman Tensor, Respectively[a]

	Parameter	AlN	GaN	ZnO	6H-SiC
(a)	$|a/b|$	2.49	1.78	0.972	1.58
	Phase difference (π)	0.507	0.487	0.480	0.479
(b)	$|a/b|$	2.46	1.77	0.984	1.57

[a](a) Traditional theory (phase difference introduced); (b) new theory (without phase difference).

that the phase difference should not be treated as an intrinsic property like the anisotropic ratio.

Substituting φ_{a-b} in Eq. (3) with $\pi/2$, and then making the traditional and new theory assume the same value, can help further figure out the role of phase difference. This theoretically proves that the so-called "phase difference" in a traditional
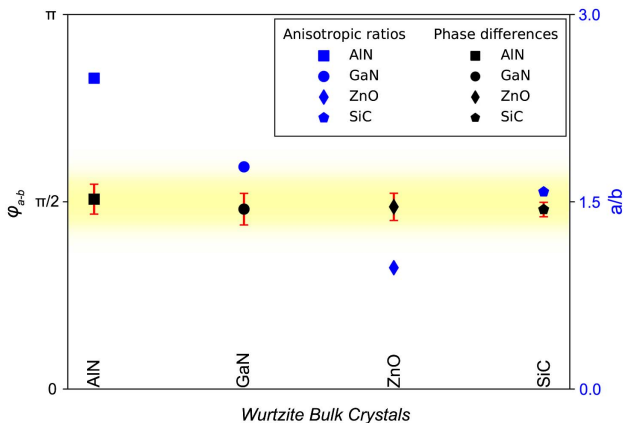

Fig. 3. Fitted phase differences and anisotropic ratios of wurtzite compounds using Eq. (3) as the Raman tensor.

Raman tensor is exactly the phase of the R_{33} element in the new Raman tensor suggested by Kranert *et al.*, and it should be set at a fixed value of $\pi/2$ in the case of bulk wurtzite compounds. Given that the $\pi/2$ phase in the new theory is attributed to the birefringence effect on optical measurement, the "phase difference" in traditional theory should actually be derived from experiments, and thus it is not tenable to view phase difference as an intrinsic property. Although both the traditional and the new theory are consistent with the experiments, the traditional theory's interpretation on phase difference is misleading. Hence, it is perfectly acceptable that the new theory should be applied in the future study of Raman tensors, without introducing "phase difference."

In the first half of this paper, the phenomenological-parameter-free Raman tensor of the A_1 phonon in bulk wurtzite crystals was given; for crystals of other structures, their Raman tensor of the A_1 phonon under the new formalism could be written as

$$\begin{bmatrix} a & & \\ & a & \\ & & be^{i\Phi} \end{bmatrix}. \qquad (8)$$

Here, Φ can be defined as an "apparent phase," given by

$$\Phi = \arccos[f(\delta, p_1, p_2, \ldots)], \qquad (9)$$

where δ is the thickness of the sample, and p_n represents the effects of detailed configuration on the Raman scattering experiment (i.e., the location relationship between experimental coordinates and the optical axis of crystals); for example, for bulk wurtzite crystals, $\Phi = \pi/2$. As is shown in Eq. (8), the expression of apparent phase contains no phenomenological parameters, which means it can be achieved through the *ab initio* method. Therefore, when using Eq. (8) in Raman tensor study, the apparent phase's value should be determined *a priori* according to a specific experimental configuration. Substituting Eq. (8) into Eq. (1) enables us to obtain the formula of the intensity-angle relationship, from which Raman tensor elements a and b can be derived according to experimental data.

3. CONCLUSION

Summarily, in traditional theory, the phenomenological phase difference (which actually should be the non-phenomenological apparent phase) was a parameter that was derived together with Raman tensor elements. Such treatment could cause uncertainties in the determination of the Raman tensor, and more seriously, the unclear phenomenon-logical parameter may also damage the clarity of the Raman tensor. This paper clarifies misunderstandings in the traditional method and further proposes the above approach. It expunges the ambiguity of physics in previous studies and enjoys a promising prospect to be applied as a general paradigm to more crystals—for example, the popular van der Waals crystals.

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