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Double resonance Raman scattering of second-order Raman modes from an individual graphite whisker

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Abstract

Resonant Raman scattering of second-order Raman modes from an individual graphite whisker synthesized by a high-temperature heat-treatment method at a special pressure was discussed here. The dependence of phonon frequencies on the incoming laser light and the frequency difference between Stokes and anti-Stokes scattering show their origin from double resonance Raman scattering. Our results show that all the experimental results of second-order Raman modes in graphite whiskers, such as the excitation-energy dependence on the mode frequency, the frequency shift between a second-order Raman mode and its fundamentals, and the frequency discrepancy between Stokes and anti-Stokes components of a second-order Raman mode can be well understood by double resonance Raman scattering.

1. Introduction

Monocrystalline graphite shows two Raman-active E_{2g} modes at 42 and 1582(G) cm^{-1} [1]. In the Raman spectra of disordered graphite, there are two additional first-order lines at ~1360 and 1620 cm^{-1}, which are often designated as the D and D′ modes [1], respectively. In the Raman spectra of graphite whiskers and multi-walled carbon nanotubes (MWNTs), two first-order (L$_1$ and L$_2$) modes are observed in the low-frequency region of 150–500 cm^{-1} [2,3]. Except two zone-center E_{2g} modes, the frequencies of other first-order Raman modes strongly depend on the excitation energy in a wide energy range [2–5]. Recently, the dispersive D mode and other first-order dispersive modes are assigned to the double resonance Raman scattering (DRRS) of the non-center phonons in several phonon branches of graphite [1,3,6–8]. The anti-Stokes double resonance Raman process of the D mode and other

first-order modes in graphite materials has also been investigated recently [3,6–9].

There exist also several dispersive second-order Raman modes in graphite materials. For example, excited with a red laser, the Raman spectra of graphite whiskers show their second-order Raman modes at about 450, 570, 1830, 1950, 2660 and 3240 cm^{-1} [2], some of which are also observed in other graphite materials [3,5,10]. According to the frequency match and the dispersive properties, these second-order Raman modes have been assigned to the overtones and combination modes of the observed first-order Raman modes. We have experimentally studied the Stokes and anti-Stokes Raman scatterings of second-order Raman modes in graphite, graphite whiskers and MWNTs [2,3,11]. The results exhibit three spectral features: (1) the frequency of a second-order mode may be unequal to the sum of the frequencies of its two fundamentals, (2) the value of the excitation-energy dependence of a second-order mode is almost equal to the sum of those of its fundamentals, (3) the frequency difference between second-order Stoke and anti-Stokes modes is determined by its peak frequency and dispersive property. The case of the

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Stokes and anti-Stokes overtone of the D mode had been discussed in detail for carbon nanotubes, two-dimensional graphite and graphite whiskers [3,8,9]. In this paper, we will discuss the double resonance Raman processes for the Stokes and anti-Stokes components of second-order modes involved two different phonons in graphite materials and explain the above experimental features of second-order modes in graphite whiskers.

2. Double resonance Raman scattering of second-order Raman modes in graphite materials

Except the Raman-active zone-center E_{2g} modes at 42 and $1582(G)$ cm^{-1}, other first-order Raman modes can be classified as two groups: one is due to an intra-valley double resonance process, such as the D′, L_1 and L_2 modes [2,3,7], the other group results from an inter-valley double resonance process, such as the D modes [1,3,6–9]. How these fundamentals contribute to the experimentally observed second-order dispersive modes? To answer this question, it is necessary to analyze the double resonance Raman process of second-order modes in graphite materials.

Here, we first focus our discussions on a second-order mode whose fundamentals just come from intra-valley double resonance processes. Saito et al. [7] had given the first discussion of the double resonance mechanism in terms of intra-valley process of the first-order dispersive modes in graphite [7]. Instead of one phonon and one defect for a first-order mode, the double resonance process of a second-order mode involves two phonons. We assume

in the later text that the frequency of the second-order mode is ω_{1+2} and this second-order mode has two fundamentals with the frequencies of ω_1 and ω_2 ($\omega_1 > \omega_2$), and δk_1 and δk_2 are two wave vectors associated with two fundamentals, $\delta k_{1,2} = \hbar\omega_{1,2}/A$, and $A = \sqrt{3}\gamma_0 a/2$, where a is graphite lattice constant and $\gamma_0 = 2.90$ eV is the tight-binding overlap integral parameter. Because the photon-excited electron in a double resonance process can be first scattered by emitting (or absorbing) a phonon of ω_1 or ω_2, there are four possible Stokes and anti-Stokes intra-valley double resonance processes for a second-order mode as shown in Fig. 1. If we neglect the trigonal warping effect [12], similar to the case of the double resonance process of a first-order mode [1,6,7], the wave vector of the fundamental ω_1 in Fig. 1(a) is determined by the electronic wave vectors of two involved resonant electronic states, $|q_1| = |2k_0 - \delta k_1|$, where the vectors $k_0 = \varepsilon_L/(2A)$ and ε_L is the laser energy. Because of the demand of the momentum conservation condition ($q_1 + q_2 = 0$), wave vector $q_2 = -q_1$ and its magnitude $|q_2| = |2k_0 - \delta k_1|$. That says that the wave vector of the fundamental ω_2 that contributes to the second-order mode ω_{1+2} is smaller than that ($|2k_0 - \delta k_2/2|$, or $|2k_0 - \delta k_2|$) of the first-order mode ω_2. For the anti-Stokes process depicted in Fig. 1(a), we can similarly determine the wave vectors of fundamentals ω_1 and ω_2 to be $|2k_0 + \delta k_1|$, and thus, the wave vector of the fundamental ω_2 that contributes to the second-order mode ω_{1+2} at the anti-Stokes side is larger than that ($|2k_0 + \delta k_2/2|$, or $|2k_0 + \delta k_2|$) of the first-order mode ω_2. The same analysis can be applied to other Stokes and anti-Stokes double resonance processes in Figs. 1(b)–(d). Several singularities
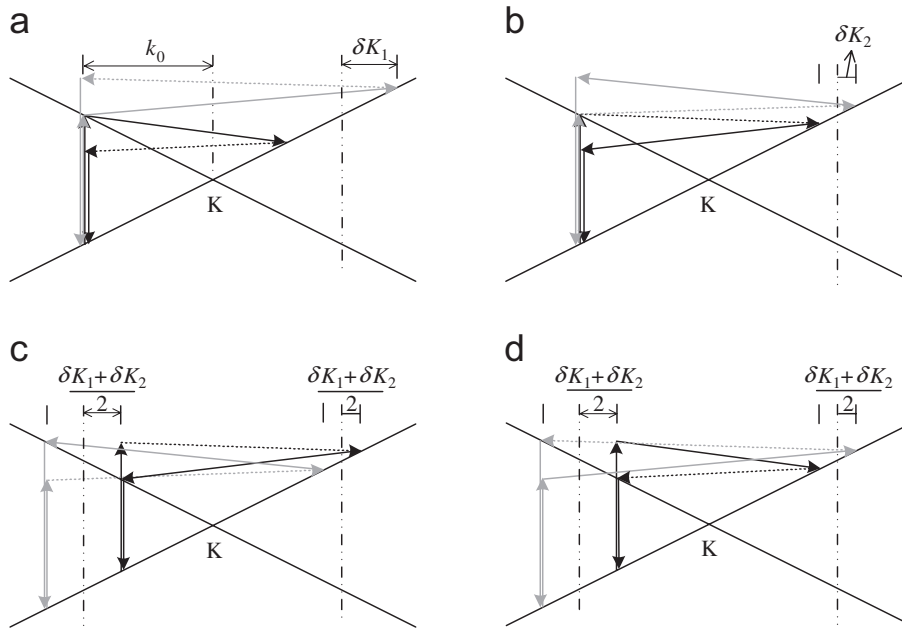

Fig. 1. Schematic diagram of four intra-valley double resonance Stokes (S, black lines) and anti-Stokes (AS, gray lines) processes for a second-order mode in graphite materials: a, inelastic scattering by ω_1 occurs first and the incident states are resonant; b, inelastic scattering by ω_2 occurs first and the incident states are resonant; c, inelastic scattering by ω_2 occurs first and the scattered states are resonant; d, inelastic scattering by ω_1 occurs first and the scattered states are resonant. Here, dashed lines show the scattered or absorbed process of the fundamental with smaller phonon energy.