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Review

Low-frequency interlayer vibration modes in two-dimensional layered materials

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HIGHLIGHTS

- The unique interlayer vibration modes in two-dimensional materials and their origins are introduced.
- The clear layer-number dependence of the interlayer modes is essential to the exact determination of thickness of few-layer flakes.
- The modes may be employed to investigate the stacking method and monitor the interlayer coupling in twisted multilayer materials and van der Waals heterojunctions.

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ABSTRACT

Two-dimensional (2D) layered materials have been attracted tremendous research interest because of their novel photoelectric properties. If a single atomic layer instead of individual atoms is taken as a rigid motion object, two unique interlayer vibrations, i.e. compression/breathing and shear motions, at ultra-low frequencies can be expected and actually have been observed in many layered materials. The vibrations stem from the interlayer van der Waals interaction and can be well described by a conventional linear-chain model in most cases. The vibration frequencies strongly depend on layer thickness, which enables an accurate determination of layer numbers. A quick and nondestructive determination of flake thickness is particularly important for the materials, since the physical properties can be dramatically changed in the cases of several atomic layers. As a measure of interlayer coupling, the low-frequency modes are also sensitive to the stacking methods of atomic layers and the overlapping of different kinds of 2D materials. This allows the modes to play a key role in the applications like van der Waals heterojunctions. In this paper, we will give a brief review on the experimental observations and theoretical understanding of the interlayer modes in several typical 2D systems, as well as their actual and potential applications.

Contents

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1. Introduction

1.1. Several typical 2D layered systems

The successive discovery of fullerene C60 and carbon nanotubes [1,2], stimulated great interest to explore the possibility of two-dimensional carbon materials. It had been predicted that 2D material does not exist in nature due to its thermal instability [3]. Until 2004, the emergence of graphene invalidated the theoretical prediction and opened the door to two-dimensional materials [4]. The sp2 hybridization and covalent in-plane σ-bonding between neighboring carbon atoms in graphene (Fig. 1a and b), provide a mechanical strength stronger than that of steel by two orders of magnitude [5–7]. Graphene only absorbs 2.3% of the incident light intensities [8,9]. It has a very high Young's modulus [10] and a thermal conductivity as high as 5300 W/m K [11]. Its electron mobility at room temperature reaches up to 200,000 $cm^2/V\,s$ [12]. These outstanding properties make graphene the most promising semiconducting material after silicon. There are two principal phonon modes in graphene, named as G and 2D bands. G band at $\sim$1580 cm^{-1} originates from in-plane vibrations of sp2-hybridized carbon atoms and has the symmetry of E_{2g}. 2D band at 2650 cm^{-1} has an almost doubled frequency of D band, which is a second-order resonance process and identified as an inter-valley scattering assisted by optical phonons and defects [13]. Therefore, 2D band is related to defects while G band is not. The lineshapes and widths of G and 2D bands depend on flake thickness, which makes the two modes as an indicator of layer number and flake quality.

Besides graphene, many other materials such as the members of graphene family (h-BN) [14], transition metal sulfides [15], transition metal oxides [16], topological insulators and some mixed phases, etc., have been prepared in 2D form [17–22]. Transition metal dichalcogenides (TMDs) refer to one hexagonal M metal atomic layer sandwiched between two hexagonal X chalcogenide atomic layers (MoS_2, for example shown in Fig. 1c and d). More than 40 graphene-like TMD layered materials can be formed through the combination of X (=S, Se and Te) and M (=Mo, W, Nb, Re, Ni and V) elements. For the 2D layered materials, a common feature is the coexistence of strong in-plane M–X–M covalent bonding and weak interlayer van der Waals force interaction (Fig. 1c and d). There are four Raman-active modes in bulk MoS_2. E_{2g}^1 mode at 385 cm^{-1} and A_{1g} mode at 410 cm^{-1} correspond to the in-plane vibrations of Mo–S bond and the out-of-plane vibrations of Mo atoms with S atoms fixed, respectively. In few-layer cases, the frequencies of the two modes exhibit an opposite evolution with flake thickness. The frequency difference between the two modes is $\sim$19 cm^{-1} in monolayer case and gradually becomes indistinguishable in five or more layer cases. This is attributed to the increasing dielectric screening and the modifications of intralayer and interlayer coupling [23]. The other TMD compounds have the similar behaviors/properties. Atomically thin TMD flakes have many outstanding advantages, like the very high on/off current ratio up to 10^6 [22]. But the relatively low mobility ($\sim$200 $cm^2/V\,s$) limits its industrial applications at present [24].

Recently layered black phosphorus (BP) has invoked enormous interest. Like other 2D materials, black phosphorus has a folded hexagonal honeycomb structure (as shown in Fig. 1e and f), with in-plane covalent bonding of phosphorus atoms and weak interlayer van der Waals force [25–27]. The main Raman modes in bulk BP are A_g^1, A_g^2 and B_{2g} [28]. A_g^1 mode at $\sim$366 cm^{-1} refers to the out-of-plane vibrations of sulfur atoms while A_g^2 ($\sim$440 cm^{-1}) and B_{2g} ($\sim$466 cm^{-1}) modes are the in-plane vibrations of sulfur atoms. A_g^1 and B_{2g} modes have little change in peak position with decreasing thickness, but the frequencies of A_g^2 mode clearly depend on layer number. BP has an adjustable direct band gap

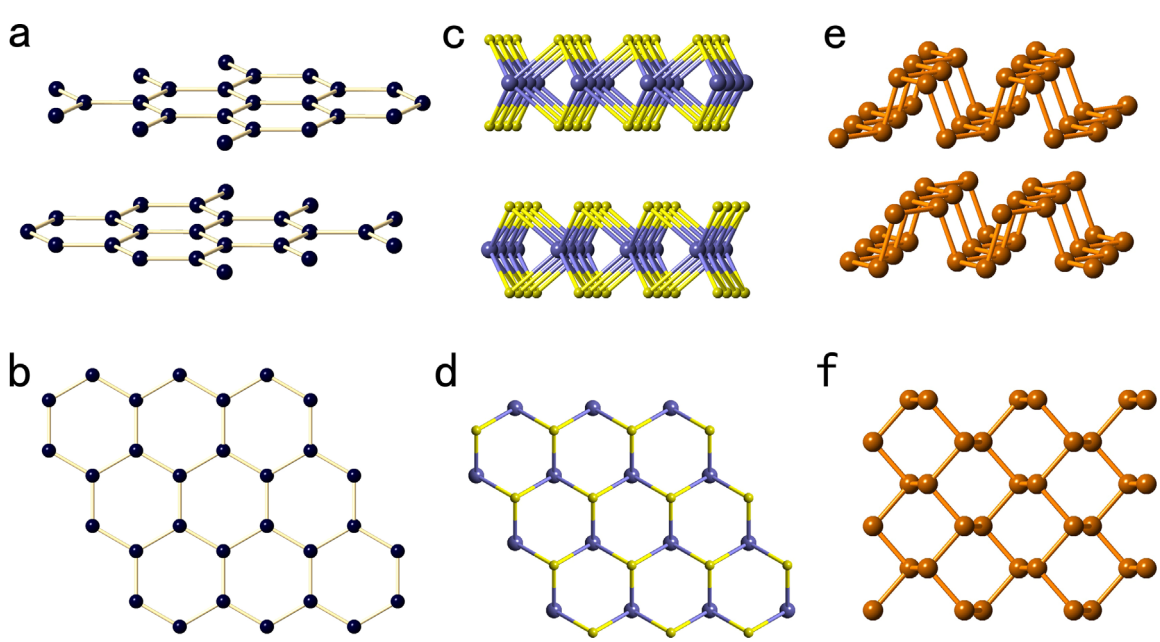

Fig. 1. (a), (c) and (e) are the side views of graphene, MoS_2 and black phosphorus lattice structures. And (b), (d) and (f) are the corresponding top views, respectively.