The role of resonant bonding in governing the thermal transport properties of two-dimensional black phosphorus

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The thermal transport properties is attracting ever much interest both for its role and relevance to practical implications, such as electronic cooling, thermoelectrics, phase change memories, such as electronic cooling, thermoelectrics, much interest both for its role and relevance to practical implications. Intrinsic phonon-phonon scattering governed by phonon anharmonicity is the key factor limiting the heat transfer ability, which is characterized by lattice thermal conductivity ($\kappa$). The wealth of fascinating phenomena arising from the phonon transport in low-dimensional open new door for the scientific understanding and technological applications opportunities of graphene and related two-dimensional (2D) materials. Phosphorene, being the single-layer counterpart of the bulk black phosphorus (BP), is an elemental 2D semiconductor with novel high carrier mobility proved by experiments and intrinsically large fundamental direct band gap in the electronic structure ($\sim 1.5$ eV). The distinctive properties of phosphorene give rise to great prospective for its applications as the active layer in nano-/opto-electronic devices, such as field-effect transistors and photo-transistor.\textsuperscript{2} The rapidly growing applications of phosphorene in nano-/opto-electronics and thermoelectrics call for fundamental understanding of the thermal transport properties, which would be of great significance to the design and development of high-performance phosphorene based nano-devices.

Herein, we provide insight into phonon transport properties of phosphorene with the deep analysis of the electronic structure and lattice dynamics. Based on the demonstration of resonant bonding formation in phosphorene, insight into the thermal transport is achieved by discussing the role of resonant bonding in driving long-range interactions and strong phonon anharmonicity. All the relevant calculations are performed based on the density functional theory (DFT) using the projector augmented wave (PAW) method as implemented in the Vienna \textit{ab initio} simulation package (\textsc{vasp}).

The concept of resonance was introduced to achieve fundamental understanding on certain properties of solids. Generally, one can construct a many-body wave function as a linear combination of different valence-bond configurations. Thus, if $\phi_1$ and $\phi_2$ are two such valence-bond configurations, the ground-state wave function $\psi$ can be expressed as

$$\psi = \frac{1}{(1 + \alpha^2)^{\frac{1}{2}}} (\phi_1 + \alpha \phi_2),$$

where the mixing coefficient $\alpha$ is determined by optimizing the binding energy or minimizing the total energy. If $\alpha$ is very small or very large, the most stable ground state is $\phi_1$ and $\phi_2$, respectively. However, in the most interesting cases where $\alpha$ is of the order of unity, the ground state involves both configurations and resonates between $\phi_1$ and $\phi_2$.

Commonly, resonance occurs where electrons are insufficient to satisfy the orbitals required for covalent bonding. Resonant bonding is formed due to the resonant orbital occupations of electrons, which is generally happenend in group IV-VI compounds with rocksalt-like structure.\textsuperscript{2} Three valence $p$ electrons are available for each atom in average. However, there are six nearest neighbours due to the rocksalt structure. Thus, the bonding configuration based on the electron occupation is not unique. The real bonding state is a hybridization among all the possible bonding configurations of the three electrons forming six bonds. We will show in the following how the resonant bonding is formed in phosphorene and its effect on the lattice dynamics properties.

The typical premonitor for the formation of resonant bonding is the weak $sp$-hybridization\textsuperscript{20}. To give a distinct view, the orbital-projected electronic structure and density of states (pDOS) ($s$, $p_x$, $p_y$ and $p_z$) of phosphorene are plotted in Fig. 1(a). The main part of $s$-orbital is confined $9$ eV below the valence band maximum (VBM), which hybridizes with $p_x$/$p_y$-$p_z$-orbital weakly. The bonding states close to the VBM are dominated by the $p_z$-orbital, forming a broad band with $\sim 6$ eV, which hybridizes with the $p_x$/$p_y$-orbitals. Due to the weak $sp$ hybridization in phosphorene [Fig. 1(a)], only three $p$ electrons are available for the bonding between $P$ atoms in phosphorene. Fig. 1(c) shows the (001) plane of phosphorus (P) in the ideal rocksalt structure. Two representative limiting configurations are shown on the left-
FIG. 1. (a) Orbital projected electronic structure and density of states (pDOS) of phosphorene. (b) Phonon dispersion with the soft TO$_{z}$ phonon branch highlighted. (c) The perspective view of the geometry structure. (d) The long-range interactions due to the resonant bonding as revealed by the perturbed charge density by atomic displacement. (e) The resonant bonding in an undistorted P phase is a hybrid form with minimized energy (middle sub-figure) of different limiting cases for bonding (left and right sub-figures). (f) The comparison of thermal conductivity ($\kappa$) among the theoretical and experimental results reported for monolayer, films with finite thickness, and bulk forms.
where the soft TO\textsubscript{z} branch is associated with strong phonon anharmonicity. Studies demonstrated that the softening of TO\textsubscript{z} phonon is based on the 1D lattice chain model\textsuperscript{12} and the large electronic polarizability can persist over long range owing to the collinear bonding due to the resonant bonding. The orbital perturbation interactions. For example, if one atom displaces along the bonding direction of the resonant bonding in the hinge-like structure of phosphorene. The microscopic picture can be intuitively understood. The resonant bonding is a superposition of different bonding configurations. Due to the more bonding than that allowed by the 8-N rule, the single, half-filled p-band forms two bonds to the left and right simultaneously. Consequently, one p-electron is shared by the two bonds, which leads to long-range interactions. For example, if one atom displaces along the +x direction due to thermal vibration, it perturbs the p\textsubscript{x} orbital of the adjacent atom. Thus, the bonding electrons of the adjacent atom on the −x side can easily move to the +x side since both sides are in the same p\textsubscript{x} orbital due to the resonant bonding. The orbital perturbation can persist over long range owing to the collinear bonding characteristics and the large electron polarizability\textsuperscript{13}.

Fig. 1(b) shows the phonon dispersion of phosphorene, where the soft TO\textsubscript{z} phonon branch with frequency decreasing around the BZ center is highlighted in red. The softness of the TO\textsubscript{z} phonon branch is due to the long-range interactions in phosphorene, which is caused by the resonant p bonding as discussed above and can be understood based on the 1D lattice chain model\textsuperscript{12}. Previous studies demonstrated that the softening of TO phonon branch is associated with strong phonon anharmonicity\textsuperscript{13} which is measured by Grüneisen parameter (γ). It has been clearly revealed that the phonon anharmonicity of the soft TO\textsubscript{z} is very strong, while those of LO\textsubscript{y} and TO\textsubscript{x} are not\textsuperscript{14}. In addition to single-layer phosphorene, the soft TO\textsubscript{z} phonon branch also exist in few-layer phosphorene.

As discussed above, resonant bonding leads to long-range interactions, softened TO\textsubscript{z} phonon branch and the corresponding strong phonon anharmonicity, which have remarkable effect on the thermal transport properties of phosphorene. For instance, due to the long-range interactions caused by the resonant bonding, interactions up to ~6 Å are still fairly strong and a large decrease of thermal conductivity of phosphorene at the cutoff distance of ~6 Å is observed. Thus, the cutoff distance should be larger than 6 Å to get satisfactorily converged results. Another interesting point is the problem of convergence/divergence with sample size (Q-grid). A not large enough cutoff distance would yield a diverged thermal conductivity\textsuperscript{10,14}. If the interactions are truncated up to 4.4 Å in phosphorene, there exists a size-dependence behavior for the thermal conductivity along the armchair direction\textsuperscript{12}. The reason for the size-dependent κ of phosphorene primarily lies in the quickly blowing up of the lifetime for phonons approaching the Γ point of the BZ. The lifetime can be effectively suppressed when long-range interactions (~6 Å) caused by the resonant bonding are involved, and then the κ of phosphorene converges.

From the thermal conductivity of single-layer [left panel of Fig. 1(f)], multi-layer phosphorene (middle panel), and bulk BP (right panel), it can be clearly observed that the thermal conductivity of phosphorene films starts from the high level of bulk BP and then decreases with thickness decreasing. It is anticipated that the thermal conductivity of single-layer phosphorene should follow the trend and being lower than the experimental results for phosphorene films with the minimized thickness of 9.5 nm (~17-18 layers). However, the results for single-layer phosphorene are only available from theoretical reports, some of which are higher than the expectation and some are lower. Due to the limitations of the synthesis technique, the results for phosphorene films with thickness smaller than 9.5 nm are currently still unavailable. The thermal conductivity of few-layer phosphorene with thinner thickness approaching to the limit of single-layer is highly expected to obtain the overall trend from bulk to single-layer and to verify the theoretical predictions.

In summary, based on the analysis of electronic structure and lattice dynamics, we provide fundamental insight into the thermal transport in phosphorene by discussing the role of resonant bonding in driving long-range interactions and strong phonon anharmonicity. We reveal that the strong phonon anharmonicity is associated with the soft transverse optical (TO) phonon modes and arises from the long-range interactions driven by the orbital governed resonant bonding. Our study highlights the physical origin of the phonon anharmonicity in phospho-
rene, and also provides new insights into phonon transport from the view of orbital states, which would be of great significance to the design and development of high-performance phosphorene based nano-devices.

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