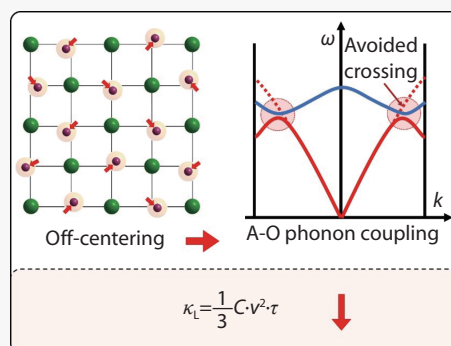


# The role of off-centering behavior and acoustic-optical phonon coupling in heat transport

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Understanding the nature of phonon transport in solids and exploring the way to minimize the thermal conductivity are important in many fields, including the development of efficient thermoelectric materials. For a long time, the contribution of optical phonons to the lattice thermal conductivity is considered to be very small and negligible. Until recent decade, a series of studies have shown that, for some materials with special electronic configuration, optical phonons can dramatically affect the lattice thermal conductivity. Specifically, in these materials, part of their cations would be off-centering from their equilibrium positions and lead to the local distortion of the coordination structure. This off-centering behavior would introduce some low-frequency optical phonons, which can couple with the acoustic phonons and cause additional phonon scattering, thus, it is very effective to suppress the lattice thermal conductivity. This perspective clarifies the lattice dynamics of off-centering behavior and illustrates how this off-centering behavior could lead to the acoustic-optical phonon coupling. This paper also demonstrates the off-centering behavior can be introduced into a material by using the lone pair element doping and the weak  $sd^3$  orbital hybridization, and proposes a strategy to design materials with low thermal conductivity based on this.



Understanding the nature of phonon transport in solids and the means to tune the thermal conductivity have been of great importance in both the science and industrial fields, particularly for thermoelectricity, where the performance of material is inversely proportional to its thermal conductivity<sup>[1-3]</sup>. Generally, the thermal conductivity of a crystalline solid includes the lattice contribution (lattice thermal conductivity,  $\kappa_L$ ) and the electronic contribution (electronic thermal conductivity,  $\kappa_e$ )<sup>[4]</sup>. For most of the semiconductors, the dominant contribution of thermal conductivity is the  $\kappa_L$ , which is usually associated with the atomic lattice and its dynamics<sup>[5]</sup>. Thus, understanding the impact of the lattice dynamics on the thermal transport is crucial for designing materials with tunable thermal conductivity that can be used in many applications<sup>[6]</sup>.

It is known that the lattice thermal conductivity of a solid can be described as:

$$\kappa_L = \frac{1}{3} \int_0^{\omega_{\max}} C_S v_g^2 \tau d\omega \quad (1)$$

where  $C_S$  is the spectral heat capacity,  $v_g$  is the group velocity, and  $\tau$  is the phonon relaxation time.<sup>[7]</sup> Comparing with the heat capacity and group velocity, the phonon relaxation time is easy to regulate. Thus far, in the field of thermoelectric materials, re-

ducing the phonon relaxation time has been considered as the most effective approach to suppress the thermal conductivity. The relaxation time expresses the time intervals between phonon collisions, and it is used to estimate the intensity of phonon scattering<sup>[8]</sup>. For a solid material, its phonon relaxation time usually includes various types of phonon scattering, and the basic scattering mechanisms are the grain boundary scattering, point defect scattering and Umklapp scattering<sup>[9]</sup>. In the past decades, many strategies have been developed to suppress the thermal conductivity *via* enhancing the phonon scattering to impede the flow of phonons. For example, introducing nanostructures to enhance the grain boundary scattering<sup>[10,11]</sup>, forming solid solutions to intensify the point defect scattering<sup>[12]</sup>, or tuning chemical bonding and anharmonicity to increase the Umklapp scattering<sup>[13]</sup>. Except for the basic scattering mechanisms, in recent years, many new-type of phonon scatterings have been proposed and demonstrated as important factor to regulate the thermal conductivity. Such as the vacancy scattering<sup>[14]</sup>, interstitial atom scattering<sup>[15]</sup>, dislocation scattering<sup>[16]</sup>, electron-phonon scattering<sup>[17]</sup> and acoustic-optical phonon scattering<sup>[18]</sup>, to name but a few. Among these, the acoustic-optical phonon scattering could be the most intriguing one.

Generally, comparing with the acoustic phonon, the phonon dispersion of optical mode is extremely flat for most of the materials. Therefore, the group velocity of optical phonons is very small, and their contribution to the lattice thermal conductivity is negligible<sup>[19]</sup>. Besides, the phonon vibration frequency of optical mode is usually much higher than that of

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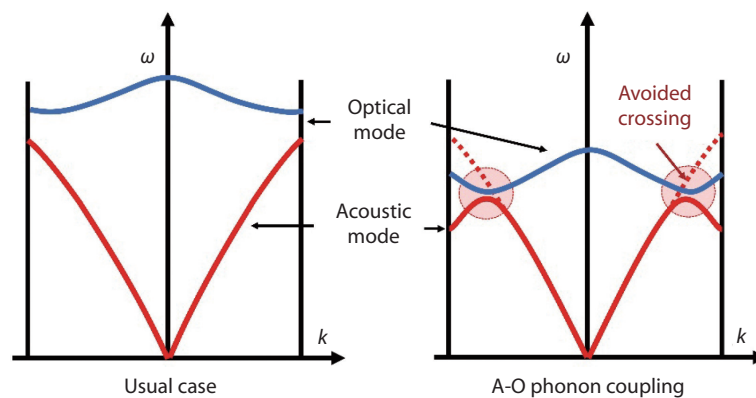
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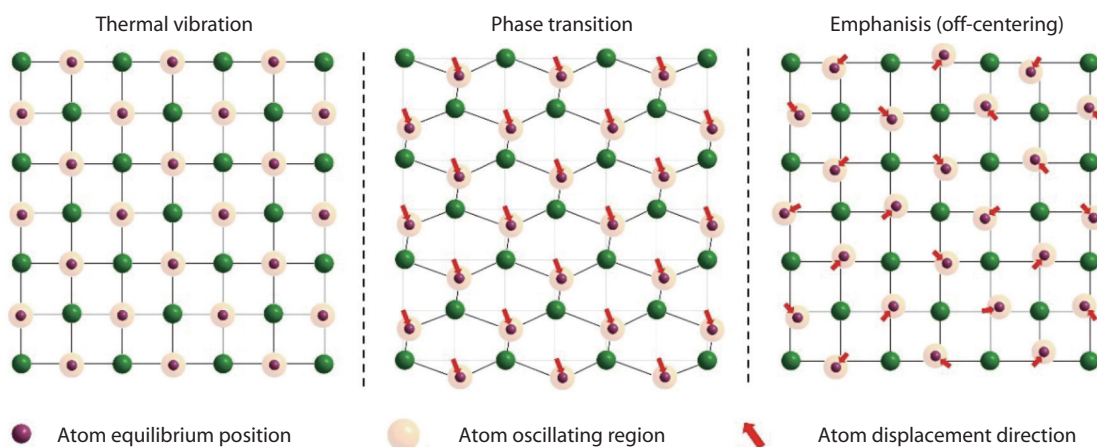
the acoustic mode, the large energy difference makes the interaction of optical phonon and acoustic phonon to be difficult, see Fig.1. Thus, optical phonon is usually excluded from the heat transport model in the classical theory. However, recent studies shown the optical phonon does in fact have significant influence on the lattice thermal conductivity, one way is through directly conducting the heat in the materials. Theoretical studies have reported over 20% of the lattice thermal conductivities for PbSe, PbTe, and CoSb<sub>3</sub> are actually contributed by the optical phonons<sup>[20]</sup>. For some special materials, such as the BaSnS<sub>2</sub>, the optical phonons are even dominant in the heat transport, which contributes over 68% of the lattice thermal conductivity<sup>[20]</sup>. Besides, optical phonons could have significant impact on the heat transport through a more common way — the acoustic-optical phonon scattering.

Recent studies shown that, for some materials with soft lattice or weak chemical bonding, some of their optical phonons could have the extremely low vibration frequency, which

sit very close to the acoustic phonons. These low frequency optical phonons can involve in the phonon scattering processes and cause additional scattering with the acoustic phonons. The avoided crossing phenomenon observed in the phonon dispersion is the characteristic feature of the acoustic-optical phonon coupling, see Fig.1. Current studies shown the weak chemical bonding is the key to bring in the acoustic-optical phonon coupling in materials, and one common way to weaken the chemical bonding is through the off-centered atom. A representative case here is the lead chalcogenides. For a long time, PbTe were believed to adopt the ideal, undistorted rock-salt structure at all temperatures. Until decade ago, Božin, Kanatzidis and Billinge had observed a local symmetry breaking in the PbTe, which, upon warming, evolves continuously from an undistorted ground state to a locally distorted state while retaining average crystallographic symmetry<sup>[21]</sup>. This unusual lattice dynamics also called emphanis- is or off-centering behavior, it is caused by the lone pair elec-



**Fig. 1** The schematic diagram shows the phonon dispersion for the usual case and the acoustic-optical (A-O) phonon coupling case. Usually, the optical modes have much higher frequency than that of the acoustic modes, and the interaction between these phonons is weak. In the A-O phonon coupling case, part of the optical phonons has the extremely low frequency, which sit very close to the acoustic mode and cause the strong interaction between these phonons. The avoided crossing phenomenon is the characteristic feature of the A-O phonon coupling.



**Fig. 2** The schematic diagram illuminates the concepts of thermal vibration, phase transition and off-centering behavior. The thermal vibration is a general effect and indicates all atoms in the crystal are dynamic variation caused by thermal energy. The phase transition indicates the atoms in the lattice move from their high energy positions to another low energy positions, their new equilibrium positions are equivalent in crystallography, and this driven by the energy and results in the global crystal symmetry breaking. However, for the off-centering behavior, the moving atoms are dynamically off-centered, and move incoherently in different directions. In this case, the local symmetry is broken, but the crystal structure still retains the original crystallographic symmetry on average.

tron of  $\text{Pb}^{2+}$  and results in its ferroelectric instability.

Hereon, to avoid any confusion of the off-centering behavior with the thermal vibration or phase transition, it is necessary to clarify the difference of these ideas. The schematic diagram in Fig. 2 illuminates the concepts of thermal vibration, phase transition and off-centering behavior. The normal thermal vibration implies all atomic movement in the crystal are dynamic variation, which is driven by thermal energy and the vibration amplitude increases with rising temperature. But the equilibrium positions of the atoms are always at the lattice centers, this is a general effect in all materials. For a traditional phase transition, when it happens, all involved atoms in the lattice would move from their high energy positions to another low energy positions. The atoms move toward the same direction and their equilibrium positions are equivalent in crystallography. This results in the global crystal symmetry breaking and the phase transition. However, in the off-centering case, the moving atoms are dynamically off-centered, and move incoherently in different directions. Therefore, their equilibrium positions are different, and the local structure is distorted, which is regarded as local symmetry breaking. However, on average, the crystal structure still retains the original crystallographic symmetry, so there is no phase transition happening.

The finding of off-centering behavior inspires researcher to further investigate the lattice dynamics and the thermal conductivity of PbTe. Researchers then realized this locally distorted state of PbTe could actually introduce some low frequency optical phonons in the material<sup>[22]</sup>. Further study identified a strong anharmonic coupling between the low frequency transverse optical modes and the longitudinal acoustic modes in PbTe via the inelastic neutron scattering measurements and the theoretical computations<sup>[23]</sup>. And the acoustic-optical phonon coupling is verified as the key to the low thermal conductivity of PbTe.

After the discovery of emphanis in PbTe, similar behaviors and acoustic-optical phonon coupling effect have been identified in more and more low thermal conductivity materials, such as the  $\text{PbQ}$ <sup>[24,25]</sup>,  $\text{SnQ}$  ( $\text{Q} = \text{S}, \text{Se}, \text{Te}$ )<sup>[26]</sup>, rock-salt  $\text{AgSbSe}_2$ <sup>[27]</sup>, cubic halide perovskites<sup>[28]</sup> and more recently, the  $\text{AgGaTe}_2$ <sup>[29]</sup>. Among these materials, the off-centering behavior of  $\text{AgGaTe}_2$  is unexpected and the most unique one. Before the discovery of  $\text{AgGaTe}_2$ , it has been believed that the off-centering behavior occurs only through the actions of the  $\text{ns}^2$  lone pair of electrons associated with main-group metals and octahedral coordination environments such as  $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$ , and  $\text{Sb}^{3+}$ . Significantly, in the  $\text{AgGaTe}_2$ , the mechanism does not involve  $\text{ns}^2$  lone pairs, and it is the first example of off-centering being observed in a tetrahedral diamondoid compound<sup>[29]</sup>. Researchers found the local structure of Ag in  $\text{AgGaTe}_2$  is distorted, and the perfect tetrahedral geometry in reality is an average of off-centering distortions occurring in a dynamic fashion. This off-centering behavior is electronic in origin, deriving from the relativistic idiosyncrasies of Ag, which results in weakened  $\text{sd}^3$  orbital hybridization. This drives Ag off its tetrahedral center and results in strong acoustic-optical phonon scattering and an ultralow thermal conductivity.

Since this effect is caused by the special electronic configuration of Ag, this implies the off-centering behavior is expected

to be observed in other silver diamondoid compounds. Thus, introducing the Ag into the tetrahedral compounds could also be an effective way to induce the off-centering behavior and suppress the thermal conductivity. In fact, the Ag-derived acoustic-optical phonon scattering has been observed in the  $\text{Cu}_{1-x}\text{Ag}_x\text{InTe}_2$ <sup>[30]</sup> and  $\text{Cu}_{1-x}\text{Ag}_x\text{GaTe}_2$ <sup>[31]</sup> alloy, and this has been considered as the root cause of the low thermal conductivity and high thermoelectric performance for these diamondoid compounds. On the other hand, based on the case of PbTe, another way to introduce the off-centering behavior into a material could be the lone pair element doping, one successful case is the In<sup>+</sup> doped  $\text{CuFeS}_2$ <sup>[32]</sup>. At this point, these findings offer a strategy for designing systems with ultralow thermal conductivity by inducing the off-centering behavior and acoustic-optical phonon coupling effect.

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## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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