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Thermal expansion induced reduction of lattice thermal conductivity in light crystals

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ABSTRACT

Combining first-principles calculations with quasiharmonic approximation and Boltzmann transport equation we take light ionic crystals LiH and NaH as examples to systematically investigate the lattice thermal properties. Remarkably, thermal expansion (TE) effect plays a significant role in heat transport of these light solids, which makes the lattice thermal conductivity κ_L reduce about 40% compared with the value excluding the TE effect. As a result, the calculated κ_L of LiH is 14.67 (12.98) $\mathrm{Wm^{-1}K^{-1}}$ at 300 (327) K, which is well consistent with the experimental value of 14.70 (12.47) $\mathrm{Wm^{-1}K^{-1}}$ at the same temperature. Our analyses reveal that the TE effect lead to the reduction of phonon frequency and group velocity, the enhancement of phonon scattering processes and scattering rate, and consequently the reduction of κ_L. These results support that TE effect is a considerable factor in calculations of κ_L in light materials.

1. Introduction

Under the background of reducing global energy consumption, the focus on thermoelectric materials has increased drastically due to their ability to capture waste heat from the transportation or the high-temperature industrial applications [1–4]. The conversion efficiency of a thermoelectric material is defined by the dimensionless figure of merit $zT = S^2\sigma T/(\kappa_L + \kappa_E)$, where S is the Seebeck coefficient, σ is the electrical conductivity, and κ_L (κ_E) is the lattice (electronic) thermal conductivity. Hence, a high power factor $S^2\sigma$ is required to improve zT whereas the thermal conductivity κ is expected to be as low as possible. In semiconductors, since κ_E is roughly proportional to σ via the Wiedemann–Franz law and often much smaller than κ_L, the reduction of κ_L becomes an important strategy to optimize thermoelectric performance [5–9].

For accurate calculation of κ_L, solving the Boltzmann transport equation (BTE) iteratively with the input parameters obtained from first-principles calculations has been proved to be a powerful approach [10–12]. To date the iterative solutions of the BTE have unveiled the lattice thermal transport properties of a great many of materials [13–20]. For instance, due to the presence of the flat Yb-dominated phonon modes, an ultralow $\kappa_L \sim 0.34$ $\mathrm{Wm^{-1}K^{-1}}$ at room temperature has been confirmed by the BTE in the fully filled skutterudite $YbFe_4Sb_{12}$ [14]; Sc_2C MXene has been claimed to possess a lowered κ_L and potential thermoelectric performance through group functionalization [16]; and the BTE result of the intrinsic κ_L for $PbTiO_3$ has been confirmed to be nearly comparable to that of good thermoelectric materials such as PbTe, which promises an excellent thermoelectric property in $PbTiO_3$ [17]. In most of these calculations, the lattice constants determined by the structural relaxation via the density functional theory (DFT) are utilized in computations of the dielectric tensor, Born effective charge, and harmonic and anharmonic interatomic force constants (IFCs) required in solutions of the BTE. However, the DFT calculated lattice constants a_0 are for the ground-state systems, which exclude the contributions from thermal expansion (TE) effect induced by the lattice vibrations. That is, to obtain a relatively accurate description for lattice thermal transport properties at finite temperature T, the TE effect induced lattice constant a_T should be applied in computations of all concerned input parameters and consequently the κ_L.

Usually, due to the light mass and strong phonon modes [30], the TE effect in light materials is relatively evident, while this effect in heavy materials is fairly weak. In this paper, we take the lightest ionic crystals LiH and NaH as examples to investigate the

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influence of the TE effect on heat transport properties, although the thermal and thermoelectric properties of them have been studied previously [18,19]. Interestingly, we find that the κ_L of LiH and NaH at room temperature reduce about 40% if the TE effect is included, with the κ_L of LiH well consistent with the experimental values. Calculation details are described in Sec. 2. The results on lattice thermal properties are presented in Sec. 3. Section 4 is our summary.

2. Methodology

Our first-principles calculations are carried out within the DFT as implemented in VASP [21,22]. The projector augmented wave potentials (PAW) is utilized to model the ion cores [23], while the valance electrons are described by a plane-wave basis set with the cutoff energy of 650 eV and the exchange-correlation functional of generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [24]. For relaxation, force criteria for the ionic step is set to be 10^{-8} eV/Å with the electronic stopping criterion of 10^{-8} eV, and a $15 \times 15 \times 15$ Γ-centered Monkhorst-Pack k-point mesh is used to simulate the Brillouin zone integration. To estimate the dielectric tensor and Born effective charges, density functional perturbation theory (DFPT) coded in VASP is utilized. The harmonic IFCs (IFC2) used in phonon calculations are generated within $5 \times 5 \times 5$ supercells by the finite-difference approach in PHONOPY program [25].

At temperature T, the equilibrium lattice constants a_T are calculated by minimization of the Helmholtz free energy $F(a_T, T)$ based on quasiharmonic approximation approach [26–28] through the PHONOPY-QHA script [29]. Retaining the harmonic expression but introducing an explicit dependence of vibration frequencies $\omega_{\mathbf{q}\nu}$ on lattice constant a_T, $F(a_T, T)$ is written as:

$$F(a_T,T)=U_0(a_T)+k_BT\sum_{\mathbf{q}\nu}ln\{1-exp[-\frac{\hbar\omega_{\mathbf{q}\nu}(a_T)}{k_BT}]\}, \qquad (1)$$

where k_B and $\hbar$ are the Boltzmann constant and reduced Planck constant, $U_0(a_T)$ is the zero-temperature internal energy which includes the DFT ground state energy $E(a_T)$ and the zero-point energy (ZPE) $E_0^{ZP}(a_T)=\sum_{\mathbf{q}\nu}\hbar\omega_{\mathbf{q}\nu}(a_T)/2$. The volumetric TE coefficient is then defined by

$$\alpha(T)=[da_T^3/dT]/a_T^3, \qquad (2)$$

where a_T is the equilibrium lattice constant at T.

From the solution of BTE [10], at the equilibrium lattice constant a_T, the lattice thermal conductivity along x direction is written as

$$\kappa_L^{xx}=\frac{1}{k_BT^2\Omega N}\sum_{\mathbf{q}\nu}f_0(f_0+1)[\hbar\omega_{\mathbf{q}\nu}(a_T)]^2v_{\mathbf{q}\nu}^{g,x}(a_T)F_{\mathbf{q}\nu}^x, \qquad (3)$$

where Ω, N, and f_0 are the volume of the unit cell, the number of $\mathbf{q}$ points in the first Brillouin zone, and the equilibrium Bose–Einstein distribution function, respectively. $v_{\mathbf{q}\nu}^{g,x}(a_T)$ is the phonon group velocity of branch ν at $\mathbf{q}$ point along the x direction. $F_{\mathbf{q}\nu}^x$ is given by

$$F_{\mathbf{q}\nu}^x=\tau_{\mathbf{q}\nu}(a_T)[v_{\mathbf{q}\nu}^{g,x}(a_T)+\Delta_{\mathbf{q}\nu}(a_T)] \qquad (4)$$

where $\tau_{\mathbf{q}\nu}(a_T)$ is the phonon lifetime in relaxation time approximation (RTA), and $\Delta_{\mathbf{q}\nu}(a_T)$ is a correction term used to eliminate the inaccuracy of RTA through solving the BTE iteratively. The ShengBTE code [10] is used to calculate the κ_L at each equilibrium lattice constant a_T. The anharmonic IFCs (IFC3) required in ShengBTE calculations are computed by VASP combined with the THIRDORDER.PY script [10], which are generated within $4 \times 4 \times 4$ supercells by the finite-difference approach in the THIRDORDER.PY script, and the interactions up to the third-nearest neighbors are included in these calculations. For BTE calculations, a q-mesh of $31 \times 31 \times 31$ is selected to simulate the Brillouin zone integration.

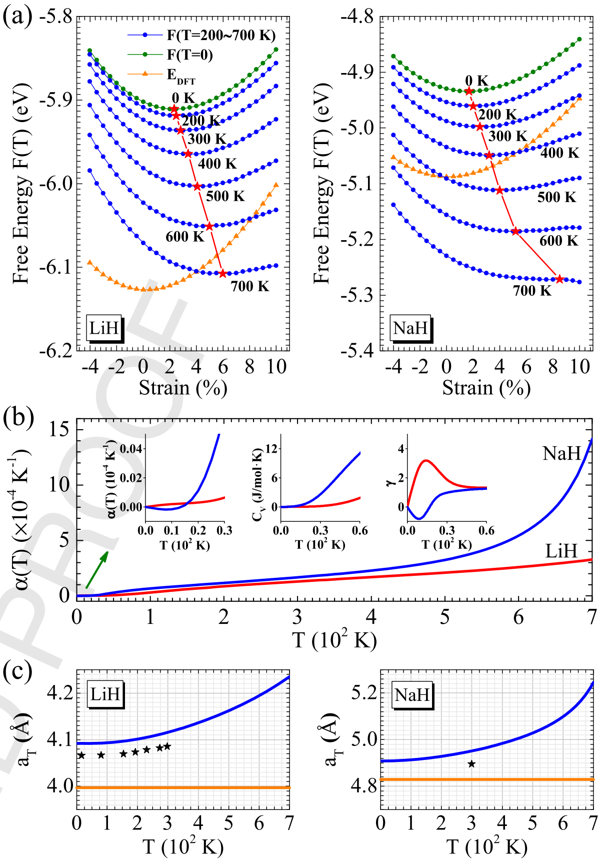

Fig. 1. (Color online). (a) Helmholtz free energies $F(T)$ of LiH (left) and NaH (right) as functions of lattice strain. The red pentagram represents the minimum value of $F(T)$ at each temperature. The orange triangle line is the DFT total energy with the minimum value at zero strain. (b) Thermal expansion coefficients $\alpha(T)$ of LiH (red line) and NaH (blue line). Insets are the zooming in of $\alpha(T)$ (left), specific heat C_V (middle), and total Gruneisen parameter γ (right) at low temperature. (c) Equilibrium lattice constants a_T versus T. The black pentagram represents the experimental values for LiH in Ref. [32] and NaH in Ref. [33]. The orange horizontal line represents the DFT lattice constant a_0.

3. Results and discussion

LiH and NaH are both rock-salt structures with the DFT lattice constants a_0 of 3.997 and 4.830 Å, respectively. The expansion of the lattice constant due to zero-point vibration is 2.32% for LiH and 1.70% for NaH, which makes the equilibrium lattice constant increase to 4.089 and 4.912 Å, respectively, as shown in Figs. 1(a) and 1(c). Obviously, due to the light mass and strong phonon modes of LiH and NaH [30], the zero-point vibrations in these materials play important roles in the lattice expansions. The temperature dependence of the TE coefficient $\alpha(T)$ is plotted in Fig. 1(b), which shows that the $\alpha(T)$ of both LiH and NaH are considerably high compared with those of most materials containing heavy elements. Overall, $\alpha(T)$ changes slowly below 40 K, and increases almost linearly from 50 to 600 K. For LiH, $\alpha(T)$ is always positive and the TE effect strengthens monotonically versus temperature T. However, the $\alpha(T)$ of NaH possesses a negative expansion below about 15 K, as shown in the insets of Fig. 1(b), which implies a slight constriction as the increase of T below 15 K. According to $\alpha(T) \propto \gamma C_V$, where γ is the total Gruneisen constant and C_V the specific heat, the negative γ and small C_V below 15 K are responsible for the slight negative expansion for NaH, as shown in the

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