High thermopower and potential thermoelectric properties of crystalline LiH and NaH

Yinchang Zhao,1,* Zhenhong Dai,1,† Chao Zhang,1 Chao Lian,2 Shuming Zeng,3,4 Geng Li,3,4 Sheng Meng,2,4,† and Jun Ni3,4,§

1Department of Physics, Yantai University, Yantai 264005, People’s Republic of China
2Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, People’s Republic of China
3State Key Laboratory of Low-Dimensional Quantum Physics, Department of Physics, Tsinghua University, Beijing 100084, People’s Republic of China
4Collaborative Innovation Center of Quantum Matter, Beijing 100084, People’s Republic of China

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We use first-principles calculations combined with the Boltzmann transport equation and semiclassical analysis to investigate the thermal conductivity \( \kappa \), electrical conductivity \( \sigma \), and thermopower \( S \) of crystalline LiH and NaH. Remarkably, the calculated \( S \) is extraordinarily high while the lattice thermal conductivity \( \kappa_L \) is fairly low, which, as a result, leads to a much high thermoelectric power factor \( \sigma S^2 \) and good thermoelectric properties, with the figure of merit \( zT \) even larger than 1.5 in the \( p \)-type doped NaH. Further analyses reveal that (i) the large band gap and the flat band around the Fermi level cause the high \( S \) and (ii) strong anharmonic phonon scatterings and relevant phonon group velocities result in the low \( \kappa_L \) in these light materials. Our results support that crystalline LiH and NaH may be potential materials for thermoelectric applications.

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I. INTRODUCTION

Thermoelectric (TE) materials have attracted great interests due to their power to convert heat into electricity, which offers a clean way to recover the waste heat from the high-temperature industrial or the transportation applications [1–4]. For a TE power generator, the conversion efficiency at temperature \( T \) is defined by the dimensionless figure of merit \( zT = \sigma S^2 T/\kappa \), where \( \sigma \) is the electrical conductivity, \( S \) is the thermopower (also known as Seebeck coefficient), and \( \kappa \) is the thermal conductivity, which consists of the lattice thermal conductivity \( \kappa_L \) and the electronic contribution \( \kappa_{el} \). Hence a complete picture to reveal TE properties requires investigating both the electronic and the thermal transport properties, while the power factor \( \sigma S^2 \) is often used to estimate the TE features. In semiconductors, because \( \kappa_{el} \) is directly related to \( \sigma \) via the Wiedemann-Franz formula \( \kappa_{el} = L \sigma T \) (\( L \) is the Lorenz number), optimization of the figure of merit \( zT \) always suffers from the interdependence between \( \sigma \) and \( \kappa_{el} \), which implies there is almost no room to tune \( \kappa_{el} \) independently. Therefore, to increase \( zT \), researchers have been turning to seek out solutions to enhance the power factor \( \sigma S^2 \) or to reduce the lattice thermal conductivity \( \kappa_L \) [5–17].

There have been many strategies proposed for the enhancement of the power factor \( \sigma S^2 \). For instance, due to a drastic improvement of \( S \) resulted from a distortion of the electronic density of states (EDOS) by the resonant impurities, a high \( zT \) of 1.5 was achieved at 773 K in the Ti-doped \( p \)-type PbTe [2,14]. The quantum confinement effect in low-dimensional Bi2Te3 caused the increase of \( zT \) by a factor of 13 over the bulk value since \( \sigma \) and \( S \) can be tuned by a highly anisotropic effective-mass tensor [15]. The maximum value of \( zT \sim 1.3 \) was obtained in Mg5Si1−xSnx solid solutions because of the conduction band convergence, which leads to a significantly enhanced \( S \) with no adverse effect on the carrier mobility [16]. In addition, \( \sigma S^2 \) can be also increased by the electron energy filtering scheme that filters out the low-energy carriers from the transport through heterostructure barriers [18,19]. As an example, in solution-processed Sn2Te3 with inserted Ag nanoparticles as nonplanar barriers, \( \sigma S^2 \) and \( zT \) were enhanced drastically owing to the carrier energy filtering effect [20].

Besides these approaches to improving TE properties, the reductions of \( \kappa_L \) have caused significant enhancements of \( zT \) via increased phonon scattering around interfaces, structural defects, and grain boundaries in the nanostructured materials [21,22]. For example, because of the significant reduction of \( \kappa_L \) to about 0.5 W m\(^{-1}\)K\(^{-1}\) via all-scale hierarchical structures, a high \( zT \) of 2.2 was reported in the bulk spark-plasma-sintered Na-doped PbTe:SrTe at 900 K [23]; a \( zT \) of 2.0 was achieved in the Na-doped PbTe at 773 K through further optimization of nanostructures to reduce \( \kappa_L \) [24]. Recently, an extraordinary \( zT \) of 2.6 was reported in the undoped monocristalline SnSe at 923 K with no nanostructuring or complex alloying but only the ultralow intrinsic \( \kappa_L \) of the crystal [25]. However, later researches reported that the \( zT \) of the doped polycrystalline SnSe is only 0.6–0.7 [26,27]. Also a theoretical study for SnSe indicated that the actual \( \kappa_L \) of the crystalline direction (\( b \) axis), along which the highest value of \( zT \) is achieved, could be higher than the \( \kappa_L \) reported in Ref. [25], which suggests a further research on the results [28]. In addition, there are a great many other materials with lower \( \kappa_L \) and good TE properties, such as CdO [11], IrSb3 [29], PbTiO3 [30], n-type TiO2 polymorphs [31], fully filled skutterudite YbFe4Sb12 [12], and nanoporous bulk silicon [13], etc. From the perspective of composition, all of these materials contain heavier atoms, which is beneficial for increasing the phonon scattering and thus helps to reduce \( \kappa_L \).

Ideally, the materials with both high \( \sigma S^2 \) and low \( \kappa \) will be the best candidates for TE applications. In this paper, we take the ultralight ionic crystal LiH and NaH as an example to
systematically investigate the thermal and electronic transport properties, and conclude that these materials have high thermopower $S$, low lattice thermal conductivity $\kappa_L$, and consequently good TE properties. Moreover, the findings for low $\kappa_L$ of these light materials are in sharp contrast with previous results that materials with lower $\kappa_L$ always possess heavier atomic masses. These results support that ionic crystal LiH and NaH are potential candidates for TE applications. Calculation details are described in Sec. II. The results on thermal and electronic transport properties are presented in Sec. III. Section IV is our summary.

II. METHODOLOGY

We study the thermal transport properties firstly. From the solution of Boltzmann transport equation (BTE) [32], the lattice thermal conductivity along the $x$ direction is defined as

$$\kappa_{Lx} = \frac{1}{k_B T^2 \Omega N} \sum_\lambda f_0 (f_0 + 1) (\hbar \omega_\lambda)^2 v_g^{x,\lambda} F_x^{\lambda},$$

(1)

where $k_B$, $\Omega$, and $N$ are the Boltzmann constant, the volume of the unit cell, and the number of $q$ points in the first Brillouin zone, respectively. $f_0$ is the equilibrium Bose-Einstein distribution function, $\omega_\lambda$ is the phonon frequency at the phonon mode $\lambda$, which consists of both the wave vector $q$ and the phonon branch $\nu$, $\hbar$ is the reduced Planck constant, and $v_g^{x,\lambda}$ is the phonon group velocity at mode $\lambda$ along the $x$ direction. $F_x^{\lambda}$ is given by [32]

$$F_x^{\lambda} = \tau_\lambda \left( v_g^{x,\lambda} + \Delta_\lambda \right),$$

(2)

where $\tau_\lambda$ is the lifetime in phonon relaxation time approximation (RTA). $\Delta_\lambda$ is a correction term which eliminates the inaccuracy of RTA by solving the BTE iteratively. If $\Delta_\lambda$ is equal to zero, the RTA result for $\kappa_{Lx}$ is obtained.

The SHENGBTE code [32] is used to calculate $\kappa_L$. The harmonic and anharmonic interatomic force constants (IFCs) required in SHENGBTE calculations are computed based on the density functional theory (DFT) software package VASP [33,34] combined with the PHONOPY program [35] and the THIRDORDER.PY script supplied with SHENGBTE, respectively. The IFC2 is generated with $5 \times 5 \times 5$ supercells by the finite-difference approach in PHONOPY. The anharmonic IFC3 is obtained with $4 \times 4 \times 4$ supercells via the same finite-difference approach in THIRDORDER.PY, and interaction up to third nearest neighbors is included in these calculations. In DFT calculations, the ion cores are modeled by the projector augmented wave potentials (PAW) [36], the valence electrons are modeled by a plane-wave basis set with the cutoff energy of 520 eV and the exchange-correlation functional of generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [37]. For relaxation of the primitive cell, the force acting on each atom is less than $10^{-8}$ eV/Å with the electronic stopping criterion of $10^{-8}$ eV. A $15 \times 15 \times 15$ $\Gamma$-centered Monkhorst-Pack $k$-point mesh is utilized to simulate the Brillouin zone integration of the primitive cell, while only the $\Gamma$ point is used for calculations of the supercells generated by the finite-difference approach. To estimate the dielectric tensor and Born effective charges required in both PHONOPY and SHENGBTE calculations, density functional perturbation theory (DFPT) coded in VASP is utilized with the $k$ mesh of $45 \times 45 \times 45$. At last, for SHENGBTE calculations, a $q$ mesh of $30 \times 30 \times 30$ is used to simulate the corresponding $q$ space integration.

To calculate $\sigma$, $S$, and $\kappa_el$, the semiclassical Boltzmann theory and the rigid-band approach implemented in the BOLTZTRAP code [38] is utilized within the constant scattering time approximation. The electronic structure is recalculated by VASP on a dense $k$ mesh of $60 \times 60 \times 60$ to obtain derivatives of the Kohn-Sham eigenvalues. The only empirical parameter in this approach is the scattering time $\tau$, which determines the value of $\sigma$ and $\kappa_el$. Experimental results on carrier concentration, mobility, and $\sigma$ can be employed to estimate $\tau$. Here, because of the lack of experimental data on conductive characters of LiH and NaH, the value of $\tau$ from 1 to 10 fs is used as a substitute.

III. RESULTS AND DISCUSSION

LiH and NaH are both rock-salt structures. Their optimized lattice constants are 4.00 and 4.83 Å, respectively, which are consistent with the experimental values of 4.08 and 4.89 Å [39–43]. The calculated phonon dispersion and phonon density of states (PDOS) of them are plotted in Fig. 1. There are six branches: two transverse acoustic (TA), one longitudinal acoustic (LA), two transverse optical (TO), and one longitudinal optical (LO) modes. The partial PDOS shows that almost all of the acoustic vibrations are afforded by the alkaline metal atoms, while most of the optical modes originate from the hydrogen atoms. The acoustic and optical branches

FIG. 1. Phonon dispersion and PDOS of LiH (a) and NaH (b). The acoustic (optical) branches arise almost completely from the vibrations of alkaline metal atoms (hydrogen atoms).
are separated by a gap of about 14.4 and 49.3 rad/ps for LiH and NaH, respectively. In polar semiconductors and ionic crystals, the optical modes always display the splitting of LO and TO around the Γ point, because of the strong coupling between the lattice and the polarization field generated by the longitudinal optical modes in the phonon long-wavelength limit. The polarization field is determined by the dielectric constants and Born effective charges calculated by DFPT in VASP. For LiH (NaH), the Born effective charges of the alkaline metal atom and the hydrogen atom are 1.02 (0.97) e and \(-1.02 (\sim 0.97)\) e, respectively, which indicates a strong polarization field, and consequently leads to a large LO/TO splitting of about 92.6 (74.5) rad/ps, as is shown in Fig. 1.

For comparison, the result of phonon dispersion for LiH is consistent with that in Ref. [44], but with higher vibration frequencies than those of LiD [44,45]. Similarly, the phonon properties of NaH are also in accordance with the previous results [46,47].

The calculated intrinsic \(\kappa_L\) of LiH and NaH with naturally occurring isotope concentrations as a function of \(T\) is plotted in Fig. 2. For LiH, since the fusing point is about 961 K [48–50], we only show the values of \(\kappa_L\) below 950 K in Fig. 2. For NaH, the decomposition temperature is about 700 K at ambient pressure [51,52], and may exceed 1000 K at high hydrogen partial pressure such as 35 MPa calculated by the Clausius-Clapeyron relation \(\log P_c m = -a/T + b\) with \(a = 5070\) and \(b = 9.49\) for pure sample [52]. Considering that the pressure of 35 MPa has almost no effect on lattice constant (\(<0.05\)%), we neglect the influence of this pressure on thermal transport, and show the \(\kappa_L\) below 1000 K for NaH in Fig. 2. The iterative solutions (ITS) of the BTE and RTA results are both shown, which reveals a difference of less than 10\% between them for \(T \geq 500\) K. Strikingly, the values of \(\kappa_L\) for these light materials are comparatively low, especially at high temperature. For instance, \(\kappa_L\) of naturally occurring NaH from the ITS (RTA) results is only 3.95 (3.65) W m\(^{-1}\) K\(^{-1}\) at 900 K, which is similar to that of CdO [11] and IrSb\(_3\) [29] at the same temperature, and approximates three to four times of the values for the representative TE materials such as PbTe and PbSe [53,54]. In addition, \(\kappa_L\) of LiH is about 50\% to 80\% higher than that of NaH as the temperature changing from 300 to 900 K. This result is much inconsistent with the mass difference of about three times between NaH and LiH, suggesting that the mass difference can not fully explain the difference of \(\kappa_L\). At 300 K, \(\kappa_L\) of LiH is 22.88 (21.80) W m\(^{-1}\) K\(^{-1}\) from the ITS (RTA) results, which is about 56\% larger than the experimental value of 14.70 W m\(^{-1}\) K\(^{-1}\) [55], but consistent with the previous calculation results [44,56], as shown in Fig. 1 in Ref. [56] and Fig. 7 in Ref. [44].

Furthermore, we also note that the isotopic effect has almost no influence in determining \(\kappa_L\) of NaH for \(T > 200\) K, while the isotopic mass variance plays a significant role in \(\kappa_L\) of LiH at the temperature below 600 K (see S1 in Ref. [57] for \(\kappa_L\) of LiH excluding isotopic effect). Therefore \(\kappa_L\) of LiH will decrease sharply if Li and H atoms are replaced by their heavier isotopes such as \(^{7}\)Li and D. For instance, \(^{7}\)LiD possesses a \(\kappa_L\) of 12.82 W m\(^{-1}\) K\(^{-1}\) at 300 K [44], which is about a half of the value for the naturally occurring case. For more details, see Ref. [44].

To reveal the detailed thermal transport mechanism, we firstly show the total relaxation times of all phonon modes as functions of frequency in Fig. 3. The total relaxation times are similar for LiH and NaH, with the relaxation times of...
the optical modes much shorter than those of the acoustic modes. This signifies that the acoustic modes are responsible for most of $\kappa_L$. Remarkably, compared with the previous TE materials, the relaxation times for the acoustic modes of LiH and NaH are fairly short, and even shorter than those of PbTe and PbSe [53], which hints a very strong phonon scattering in these light materials. In addition, precise comparison shows that for most of the TA, LA, and LO modes, the relaxation time of LiH is shorter than that of NaH, while for the TO modes, LiH possesses a longer relaxation time. In addition, precise comparison shows that for most of the TA, LA, and LO modes, the relaxation time of LiH is shorter than that of NaH, while for the TO modes, LiH possesses a longer relaxation time. In addition, precise comparison shows that for most of the TA, LA, and LO modes, the relaxation time of LiH is shorter than that of NaH, while for the TO modes, LiH possesses a longer relaxation time. In SHENGTE calculations, due to the exclusion of boundary scattering effect, the total relaxation time in RTA is obtained by anharmonic three-phonon scattering and isotopic scattering through the relation of $1/\tau_\lambda = 1/\tau_\lambda^{\text{anh}} + 1/\tau_\lambda^{\text{iso}}$. $1/\tau_\lambda^{\text{anh}}$ can be obtained by the sum of the three-phonon transition probabilities $\Gamma_{\lambda,\lambda',\lambda''}^{\text{anh}}$, which is determined by the anharmonic IFC3 and the weighted phase space $W$ (a direct measure of the number of scattering processes) [12,58]. Our results show that compared with NaH, LiH possesses a stronger three-phonon scattering (see S2 in Ref. [57]), while it has a smaller weighted phase space $W$ (see S3 in Ref. [57]). The smaller $W$ corresponds to less three-phonon scattering channels, which seems to be contradictory with the stronger anharmonicity of LiH. To explain this, we calculate the $\kappa_L$ of a hypothetical LiH (NaH), whose IFC3 is replaced by that of NaH (LiH), while all the other quantities remain the same. The result is 55.33 (4.77) W m$^{-1}$ K$^{-1}$ for the hypothetical LiH (NaH) at 300 K, in sharp contrast to 22.88 (15.41) W m$^{-1}$ K$^{-1}$ for the genuine one at the same temperature. This means that the IFC3 of LiH is much stronger than that of NaH, which is the main reason for the difference of anharmonicity between LiH and NaH. In addition, the isotopic scattering in LiH is also stronger than that in NaH (see S4 in Ref. [57]), which explains the importance of isotopic effect in calculations of $\kappa_L$ for LiH. The finding is consistent with a stronger isotopic effect of Li atom which, with respect to Na atom, have the features of lighter atomic mass, more stable isotopes, and considerable abundance of each isotope. However, it is worth noting that the strong anharmonic three-phonon scattering is the main reason for the lower $\kappa_L$ in these light materials, even in LiH at lower temperature. For example, the calculated $\kappa_L$ of LiH with only anharmonic scattering is 30.95 W m$^{-1}$ K$^{-1}$ at 300 K, indicating that the anharmonic scattering takes up about 74% of the total scattering at this temperature. Finally, one can conclude that LiH possesses a relatively short total relaxation time compared to NaH.

The higher $\kappa_L$ of LiH seems to be contradictory with the shorter total relaxation time in it. To further study the difference of $\kappa_L$ between LiH and NaH, we show the phonon group velocities within the whole first Brillouin zone in Fig. 4. The phonon group velocities for the nth branch are determined by $v_g = d\omega_n/dq$. With heavier atomic mass, NaH has much smaller group velocities than LiH, especially the group velocities for the acoustic branches. For the TA and LA modes, the maximum group velocities of LiH are about 7.96 and 11.41 km/s, respectively, while those of NaH are about 3.85 and 6.09 km/s, respectively. For the optical modes, LiH and NaH have almost the same group velocities with the maximum values of about 6.50 km/s for the TO modes and 5.50 km/s for the LO modes. In view of $\kappa_L \sim v_g^2$ in RTA, these findings support there exists a higher $\kappa_L$ in LiH, as is shown in Fig. 2. Noticeably, the maximum group velocities of NaH are about twice of those of PbTe and PbSe [53]. This is the primary factor that results in $\kappa_L$ of NaH being higher than those of PbTe and PbSe. Furthermore, from the group velocities combined with the relaxation time, we can also analyze the polarization dependent $\kappa_L$. We find that for NaH the optical modes have almost no contribution to $\kappa_L$, while for LiH the TO$_2$ modes contribute about 9% of the total $\kappa_L$ due to their longer relaxation time (see S5 in Ref. [57] for the polarization dependent $\kappa_L$).

In addition, we have also calculated the cumulative thermal conductivity $\kappa_C$ with respect to the allowed phonon maximum mean-free path (MFP) to study the size dependence of $\kappa_L$. $\kappa_C$ of LiH and NaH at 300 K are plotted in the inset of Fig. 2. The total accumulation keeps increasing as MFPs increases, until reaching the plateau after MFPs increase to 140 nm and 290 nm for LiH and NaH, respectively. The maximum MFPs in LiH and NaH are much longer than those in PbSe and PbTe [53], which is consistent with the high group velocities of these light materials. Furthermore, phonons with MFPs shorter than 100 nm contribute about 80% of the total $\kappa_L$ for LiH and around 84% for NaH. This means that the nanostructuring with the length of 100 nm would reduce $\kappa_L$ by 20% for LiH and 16% for NaH. Thus, to significantly reduce $\kappa_L$ of these materials, nanostructures with the characteristic length shorter than 100 nm are required.
CBM of LiH is formed from the $p$ orbitals of the alkaline atoms, in contrast with the $s$ orbitals of the alkaline atoms composing the CBM of NaH. Prominently, the band gaps of 2.96 and 3.75 eV for LiH and NaH are much larger than the gaps of most of the known TE materials. Usually, the large band gaps guarantee the high specific heats of carriers, which is a part of reasons why the best TE candidates are mostly semiconductors [1]. We also note that there is a comparatively small dispersion in the valence band, which makes the band around the VBM be fairly flat. Correspondingly, the total EDOS increases very rapidly just below the VBM, especially for NaH. For instance, the EDOS reaches nearly 1.8 states/(eV cell) only at 150 meV below the VBM in NaH. This behavior of valence band implies that there is a large effective mass of electron in LiH and NaH. As is well known, at the constant carrier concentration, the thermopower $S$ is proportional to the effective mass. Thus, high thermopower $S$ is expected in LiH and NaH. In addition, to further understand the behavior of band just below the VBM, we also check the isoenergy (Fermi surface) of the zero temperature LiH and NaH for Fermi level $E_F$ taken a little into the valence band. At 100 meV below the VBM, we find that LiH possesses a two-dimensional Fermi sheet centered at the X point, while NaH has a cylinderlike feature along the high-symmetry lines WU and WK in view of the periodicity of the Brillouin zone, see Figs. 5(c) and 5(d). This interprets the quasi step function EDOS in NaH considering that the strictly two-dimensional cylinder has a step function EDOS. Similar feature was also detected at 250 meV below the VBM in PbTe [61]. Compared with PbTe, the cylinderlike feature in NaH is more close to the VBM, which is expected to be beneficial for further improving the TE performance.

To assess the electronic transport and TE properties quantitatively, we use the BOLTZTRAP code to calculate the thermopower $S$ and the electrical conductivity $\sigma/\tau$ as functions of temperature $T$ and doping concentration $n$ for LiH and NaH. All of these calculations are checked by the POSTW90.X program of the WANNIER90 code [62,63], and consistent results are obtained. The calculations with the scissors shift of 2.00 and 2.10 eV for LiH and NaH are also performed, which shows that band gap underestimate have no effect on the thermopower $S$ and electrical conductivity $\sigma/\tau$. Our results show that the best TE performance is obtained in NaH with the $p$-type doping, while other cases such as the $n$-type doped NaH and the $p$-type doped LiH also show good TE properties. The calculated $S$ and $\sigma/\tau$ as functions of $T$ and $n$ for the $p$-type doped NaH are plotted in Figs. 6(a) and 6(b), respectively. Being consistent with the electronic Boltzmann theory [38], the $\sigma/\tau$ curve does not depend on $T$, and increases with the doping concentration $n$. The thermopower $S$ increases with $T$ at the same $n$, and decreases with $n$ at the same $T$, similar to the observed tendency in most of semiconducting TE materials. Strikingly, $S$ is extraordinarily high, as is expected in the band structure analyses. For instance, the values of $S$ for NaH are in the range of 2.22 × 10⁻¹⁰ to 2.85 × 10⁻⁴ V K⁻¹ as $T$ increases from 500 to 1000 K at $n \sim 1.0 \times 10^{31}$ cm⁻³, as shown in Fig. 6(a). If the doping concentration lowers, $S$ can be further improved, such as 4.06 × 10⁻⁴ V K⁻¹ with $n \sim 1.0 \times 10^{30}$ cm⁻³ at $T = 500$ K. These values of $S$ are much higher than that of PbTe, as shown in Fig. 3 in Ref. [2]. Combined with that the typical $S$ for a high-$zT$ material varies...
between $2.00 \times 10^{-4}$ and $3.00 \times 10^{-4}$ V K$^{-1}$, these results suggest a possible high $zT$ in NaH, although the exact value of $\sigma$ cannot be confirmed at present.

To calculate $\sigma$, we firstly use a simple formula $\tau \sim d/v$ to roughly estimate the amplitude of electronic scattering time $\tau$, where $d$ is the average electron-electron distance estimated by the doping concentration, $v = \frac{1}{\hbar} \partial E / \partial k$ is the corresponding electron velocity. From the positive doping concentration $n \sim 10^{21}$ cm$^{-3}$ and the electron velocity $v \sim 10^5$ m/s at this doping level in NaH, $\tau$ is found to be about 10 fs. Given the effect of lattice vibration on practical $\tau$, here we use the value of $\tau$ from 1 to 10 fs as a substitute in calculations of $\sigma$ and $\kappa_el$. In order to obtain a more relevant $zT$, the electronic thermal conductivity $\kappa_el$ is also included, although it is small compared to $\kappa_l$, as shown in Fig. 6(d). Our calculations show that at high temperature $zT$ for the $p$-type doped NaH often exceeds 1.0 as $\tau$ varies between 1 and 10 fs, as shown in Fig. 6(e). With $\tau = 5$ fs, a fairly large $\sigma S^2 \sim 0.79 \times 10^{-2}$ Wm$^{-1}$K$^{-2}$ and a high $zT \sim 1.53$ are achieved at $T = 1000$ K and $n \sim 1.4 \times 10^{21}$ cm$^{-3}$, as shown in Figs. 6(c) and 6(e). As $\tau$ increases to 10 fs, an extraordinarily high $zT \sim 2.39$ can be reached at $n \sim 1.0 \times 10^{21}$ cm$^{-3}$, while a maximum $zT$ of 0.60 is obtained at a higher $n$ if $\tau$ lowers to only 1 fs, as shown in Fig. 6(e). In addition, for the $p$-type doped LiH, the maximum $zT$ of 0.82 and 1.35 are obtained at $T = 900$ K with $\tau = 5$ and 10 fs, respectively (see S6 in Ref. [57]). Besides the $p$-type doping, the cases with $n$-type doping may also show good TE performance. For example, the maximum $zT$ of 0.82 and 1.28 are achieved in NaH at $T = 1000$ K with $\tau = 5$ and 10 fs, respectively (see S7 in Ref. [57]). By using $zT \geq 1.0$ as a criterion, we also check the suitable work temperature for LiH and NaH. With $\tau = 5$ fs, only the $p$-type doped NaH at $T \geq 800$ K meets this criterion. With $\tau = 10$ fs, the temperature leading to $zT \geq 1.0$ in the $p$-type doped NaH decreases into about 650 K, while the $p$-type doped LiH and $n$-type doped NaH need $T \geq 830$ and 840 K, respectively, to meet this requirement. As an example, see $zT$ of the $p$-type doped NaH at different temperature in S8 in Ref. [57]. In addition, for the $p$-type doped NaH, $n \sim 1.0 \times 10^{21}$ cm$^{-3}$ corresponds to about 0.028 holes per primitive cell, which can be realized theoretically by creating a Na vacancy in 36 unit cells. However, due to the tendency toward decomposition into metal Na and H$_2$ at high temperature, NaH tends to produce NaH$^-$ by creating a Na vacancy in 36 unit cells. However, this result can not be confirmed at present.

FIG. 6. TE parameters for the $p$-type doped NaH: (a) Thermopower $S$ at 300 to 1000 K. (b) Electrical conductivity $\sigma/\tau$. (c) Power factor $\sigma S^2$. (d) Total thermal conductivity $\kappa$ (full lines) and electronic thermal conductivity $\kappa_el$ (dash lines). (e) Figure of merit $zT$. In (c)–(e), the curves and the upper and lower limits of the vertical bars represent the values at 1000 K with $\tau = 5$, 10, and 1 fs, respectively.
a stronger anharmonicity, and thus complies with the results of the strong anharmonic three-phonon scattering. Notably, at finite temperature, the effect of external pressure is naturally included in these calculations because thermal expansion can not be captured in the MD simulations with invariant supercell, which not only explains the good structural stability of NaH at high temperature but also shows the significant role of external pressure on the stability.

Finally, it is worth to note that it is challengeable to realize TE performance in these light materials at ambient conditions, especially in NaH, because the chemical properties of these materials are fairly active [52,64]. However, at rigid conditions such as water proofing, air proofing, and light shading, TE applications of LiH is probable to be realized. For NaH, to prevent the decomposition at high temperature, the additional conditions such as high purity of sample and partial pressure above 35 MPa are also acquired to realize TE performance [52]. Although these conditions put forward enormous challenges in design of TE power generator, our calculations support that LiH and NaH are potential TE materials at suitable surroundings.

IV. CONCLUSION

In summary, we have used the Boltzmann transport theory together with first-principles calculations to compute the lattice thermal conductivity $\kappa_L$ of LiH and NaH. We discover that the calculated $\kappa_L$ of these light materials are fairly low. Further analyses reveal that the strong anharmonic phonon scattering and the relevant phonon group velocities lead to the low $\kappa_L$. A stronger anharmonic phonon scattering is found in LiH, owing to the stronger anharmonic IFC3 of LiH than that of NaH. But a lower $\kappa_L$ was obtained in NaH because of the much smaller group velocities compared to those in LiH. Then we use a combination of the semiclassical analysis and first-principles calculations to study the thermopower $S$ and electrical conductivity $\sigma/\tau$ of these materials, and conclude that due to the large band gaps and flat band around the Fermi level, $S$ of these materials is extraordinarily high. As a result, a high power factor $\sigma S^2$ is obtained in LiH and NaH. As the electronic scattering time $\tau$ varies between 1 and 10 fs, the figure of merit $\zeta T$ for these materials is often larger than 1.0. Remarkably, a high $\zeta T = 1.53$ is achieved in the $p$-type doped NaH with $\tau = 5$ fs, and a superhigh $\zeta T \sim 2.39$ is obtained in the same NaH with $\tau = 10$ fs. At last, we also carried out a molecular dynamics to confirm the stabilities of LiH and NaH, and found that the pure LiH and NaH are both stable at high temperature. In addition, a relatively large bond fluctuation around the balanceable bond lengths also implies the strong anharmonic three-phonon scattering in these materials. These theoretical results support that crystalline LiH and NaH may be potential materials for thermoelectric applications at suitable conditions such as water proofing, air proofing, light shading, high pressure, and high purity of sample, etc.

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