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Determining factors of thermoelectric properties of semiconductor nanowires

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Abstract

It is widely accepted that low dimensionality of semiconductor heterostructures and nanostructures can significantly improve their thermoelectric efficiency. However, what is less well understood is the precise role of electronic and lattice transport coefficients in the improvement. We differentiate and analyze the electronic and lattice contributions to the enhancement by using a nearly parameter-free theory of the thermoelectric properties of semiconductor nanowires. By combining molecular dynamics, density functional theory, and Boltzmann transport theory methods, we provide a complete picture for the competing factors of thermoelectric figure of merit. As an example, we study the thermoelectric properties of ZnO and Si nanowires. We find that the figure of merit can be increased as much as 30 times in 8-Å-diameter ZnO nanowires and 20 times in 12-Å-diameter Si nanowires, compared with the bulk. Decoupling of thermoelectric contributions reveals that the reduction of lattice thermal conductivity is the predominant factor in the improvement of thermoelectric properties in nanowires. While the lattice contribution to the efficiency enhancement consistently becomes larger with decreasing size of nanowires, the electronic contribution is relatively small in ZnO and disadvantageous in Si.

Introduction

Using nanostructures for thermoelectric (TE) materials is a promising prospect as it opens up a possibility of controlling the TE properties by modifying the size and shape, in addition to the composition of the material. The TE properties of a material are characterized by a dimensionless figure of merit, $ZT = TS^2\sigma/(\kappa_e + \kappa_l)$, where T , S , σ , κ_e , and κ_l are temperature, Seebeck coefficient (thermopower), electrical conductivity, electronic thermal conductivity, and lattice thermal conductivity, respectively. The main issue in finding large ZT materials is to balance the advantageous material properties, i.e., S and σ , with the detrimental κ_l and κ_e . The S , σ , and κ_e are related to the electronic states and cannot be controlled independently in bulk materials. The κ_l of bulk materials is a structural property that is also difficult to manipulate. It was suggested that reduction of the dimensionality should provide certain controllability over the individual transport coefficients, leading to a dramatic increase in ZT [1]. $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ epitaxial superlattices were reported to exhibit a very high ZT of 2.4 at

room temperature [2], larger than the maximum ZT of 1.14 for a p -type $(\text{Bi}_2\text{Te}_3)_{0.25}(\text{Sb}_2\text{Te}_3)_{0.72}(\text{Sb}_2\text{Se}_3)_{0.03}$ alloy at room temperature [3], affirming the basic premise. In many cases, however, the decrease in phonon transport also leads to the reduction in power factor due to decrease in electron transport. The search for the balance between these factors is currently ongoing.

In this letter, we report the results of a theoretical investigation of TE properties of semiconductor nanowires to provide a microscopic picture for key contributing factors to improve the TE performance of nanostructures. The focus of this work is to distinguish electronic and lattice contributions to the enhancement of ZT in nanowires (NWs) by means of parameter-free calculations. Previous theoretical studies have provided proof-of-principle verification of ZT improvement in nanostructures [4,5], but their analyses were based on the lattice thermal conductivity speculated from the bulk value. By combining molecular dynamics (MD), density functional theory (DFT), and Boltzmann transport equation (BTE) methods, we compute all of the transport coefficients without empirical parameters.

Methods of calculations

In this work, we used equilibrium MD simulations based on Green-Kubo formula, using LAMMPS [6,7] code to

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compute lattice part of thermal conductivity. The interatomic interactions in ZnO are modeled using the Buckingham potential with long-range Coulomb interactions [8,9]. This potential has been applied to describe elastic properties of ZnO nanostructures [10], their structural transformations [11,12], and thermal properties [13-15]. In case of Si NW, we used Stillinger-Weber [16] potential, which has been applied to model thermoelectric properties of Si both in the bulk and on the nanoscale [17,18]. The atomic and electronic structures of ZnO NW were calculated using planewave DFT method implemented in VASP code [19]. We used the generalized gradient approximation with Perdew-Burke-Ernzerhof exchange-correlation functional [20]. The k -point grid of $4 \times 4 \times 24$ and an energy cutoff of 400 eV were used for all calculations. The TE coefficients of ZnO nanowires were calculated based on Boltzmann transport theory, using BoltzTraP [21]. The method calculates TE properties using the result of *ab initio* electronic structure method results. Within this semi-classical method, the group velocity and the mass tensor are calculated using the DFT band dispersion. Assuming a constant carrier relaxation time, one can calculate the TE coefficients from the transport tensors [22].

The only physical parameter that we do not seek to calculate from first principles is the relaxation time, τ . It is a complex function of atomic and electronic structure, temperature, impurities, and carrier concentrations. Experimentally, it has been reported that the carrier relaxation time in ZnO nanowires is close to the bulk relaxation time. The time-resolved terahertz spectroscopy measurements of electron conductivity yielded the relaxation time of 28 and 35 fs for 500-nm radius nanowires and films, respectively, at the electron density of 10^{17} cm^{-3} [23]. Throughout this paper, we adopt the ZnO bulk relaxation time $\tau = 30$ fs for our calculations. The relaxation time in NW is generally larger than in the bulk [4], and therefore, our estimation of τ represents a correct quantitative picture. In the case of Si NW, we also used the carrier concentration-dependent τ fitted into the experimental data [24].

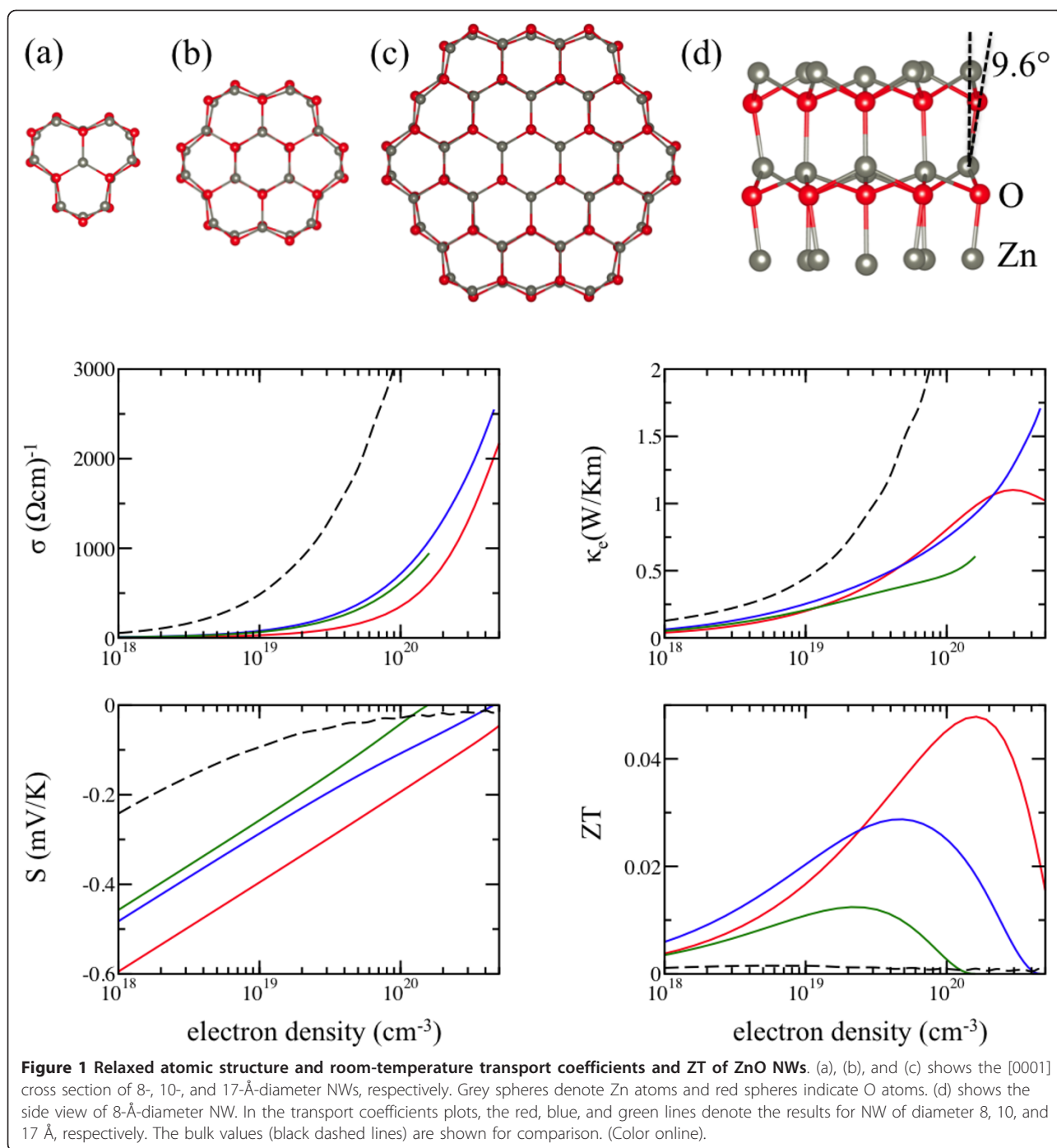
Results and discussion

When the ZnO NW is grown in [0001] direction, the surface oxygen atoms move outward away from the nanowire center while the zinc atoms moving inward toward the center (Figure 1 (a-d)). This “buckling” of the surface atoms has been reported in elastic low-energy diffraction experiments, where Zn-O bonding on the surface of ZnO (10-10) is tilted by an angle of 12° from the [0001] axis [25]. In our calculations, the tilting angle is 9.6° , in agreement with previous DFT results [26]. We also find that the bond length of the O-Zn surface dimer is reduced from 2.07 to 1.9 Å (similar to Ref. [27]). This

surface reconstruction removes the surface states from the nanowire band gap. The computed electronic band gaps are 1.65, 1.47, and 1.13 eV for 8, 10, and 17 Å NWs, showing gap opening due to the quantum confinement. In comparison, the bulk ZnO band gap in our calculations is 0.73 eV.

The electronic structure and thermoelectric properties of Si [001] NW were computed for comparison. The diameter of the NW was 12 Å with single-bonded surface atoms removed and the surface atoms passivated by hydrogen to remove dangling bonds (inset to Figure 3). The computed band gap in the Si NW was 2.11 eV, in comparison with computed 0.56 eV in the bulk. The electronic properties of Si NWs have been studied in great detail in the past [28]. Electronic part of thermoelectric properties has also been addressed previously [4], suggesting improvement of ZT to as large as 1.55. However, the lattice thermal conductivity in these calculations was presumed instead of being calculated. The significance of the lattice conductivity is discussed below.

The heat transport through the phonon channels in nanowires is analyzed here via the classical MD simulations. The atomic structures for ZnO NWs used in MD calculations are the same as in the electronic part calculations, with their dimension in [0001] direction extended to 50 Å. Using periodic boundary conditions in this directions, our tests show that for these NWs, the effects of finite length are negligible. The value of the lattice thermal conductivity is the averaged integral of the heat current autocorrelation function (ACF). In bulk ZnO and ZnO NWs, the heat current ACF exhibits strong oscillations due to zero wave vector optical phonon modes. For example, ACF for the 8 Å ZnO NW shows a 56.7-meV phonon mode, which agrees well with the energy (approximately 53 meV) of the optical branch at the Γ -point for bulk wurtzite ZnO [29]. Although these optical phonon oscillations do not contribute to the heat current, they significantly complicate the numerical integration of the heat current ACF [30]. To avoid numerical instabilities due to this optical phonon mode, a very small MD step of 0.1 fs was taken in our MD calculations. κ_l were averaged over the total MD run times of 3 ns. At room temperature, the experimental κ_l of bulk ZnO varies from about 50 to 140 W/Km [31,32], depending on growth conditions. The bulk values of $\kappa_l = 85$ W/Km in [0001] direction were obtained by extrapolating to infinity the results for a series of simulation box sizes. For the NWs, a significant reduction in κ_l is obtained. The converged values of the κ_l at room temperature are 7.9, 9.2, and 11.7 W/Km for 8, 10, and 17 Å NWs, respectively. In case of Si NW, there are no optical phonon oscillations in the ACF and computing κ_l is relatively straightforward. In the bulk Si, we obtain $\kappa_l = 254$ W/Km at room temperature. This value is overestimated by



about 70% in comparison with experiment, which is typical for Stillinger-Weber potential. In the 12 Å Si NWs, κ_l is reduced to 2.8 W/Km. This value is close to the presumed lattice thermal conductivity in the previous study by Vo et al. [4]. This reduction of κ_l can stem from several processes, such as three-phonon Umklapp, mass difference, and boundary/surface scattering. In ZnO and Si NWs considered here, the primary process is likely the increased surface phonon scattering, evident from the

fact that κ_l decreases with increasing surface to volume ratio.

The calculated TE properties of ZnO NWs at room temperature are shown in Figure 1 as a function of carrier concentration. Compared with the bulk TE coefficients, σ changes are unfavorable to the ZT while S and κ_e change positively. Notice that the unfavorable change in σ is much larger than the favorable increase in the magnitude of S , but the quadratic dependence of ZT on

S nearly cancels the effect of linear dependence on σ . The combination of these changes, together with the change in κ_l , conspires a significantly improved ZT in NWs. The changes of individual TE transport coefficients are consistent with the tendencies found in previous calculations of Si NW [4], nanoporous Si [5], and Si NW computed here (not shown). The maximum ZT is more than 30 and 20 times larger than that of the bulk in ZnO and Si, respectively, confirming the basic proposition of ZT enhancement in nanostructures. However, both Si and ZnO nanowires considered here are ultra thin; therefore, these results represent the largest values for ZT enhancements possible solely due to scaling down the sizes and using these materials on the nanoscale.

To distinguish the electronic and lattice contribution to the improvement of ZT separately, we computed the ZT of NWs using the lattice thermal conductivity of bulk ZnO, κ_l^{bulk} , and that of NWs, κ_l^{MD} . The top panel of Figure 2 shows the ZT of ZnO NW using κ_l^{MD} of each NW and the bottom panel shows the ZT using κ_l^{bulk} . While a large enhancement of maximum ZT in NW has contributions from both electronic and lattice part (top panel), the increase in ZT at the bottom panel stems solely from the changes in the electronic structure. In Table 1 we show the ratio of the maximum figure-of-

merit of nanowire, ZT^* , to the bulk counterpart, ZT^*_{bulk} : $\zeta = ZT^*/ZT^*_{\text{bulk}}$. The enhancement of ZT due to the changes in electronic structure can be parameterized by $\zeta_e = ZT^*(\kappa_l^{\text{bulk}})/ZT^*_{\text{bulk}}$, where $ZT^*(\kappa_l^{\text{bulk}})$ is the ZT of NWs calculated using the bulk lattice thermal conductivity. It appears that the quantum confinement has only modest effects, i.e., $\zeta_e = 3.25, 2.15,$ and 1.15 for 8, 10, and 17 Å nanowires, respectively. The remaining contribution of ζ comes from the lattice part, $\zeta_l = \zeta/\zeta_e$. We see a much larger effect of lattice contribution, i.e., $\zeta_l = 9.69, 8.79,$ and 7.10 for the same set of NWs. We also observe that both contributions of the electronic and the lattice part to the enhancement of ZT decrease as the diameter of the NW increases. In particular, the electronic contribution to the ZT enhancement becomes negligible when the NW diameter is as large as 17 Å.

This enhancement of ZT due to the reduction of the lattice thermal conductivity is even more pronounced in Si NWs (Figure 3). As presented in Table 1 the changes in the electronic structure on the nanoscale lead to the reduction of ZT by nearly a factor of 4, with $\zeta_e = 0.264$, in contrast to those of ZnO. This reduction stems from the decreased electric conductivity in comparison with the bulk. The thermopower, on the other hand, remains relatively unchanged. As a result, the power factor in Si nanowires is about 4.6 times smaller than that in the

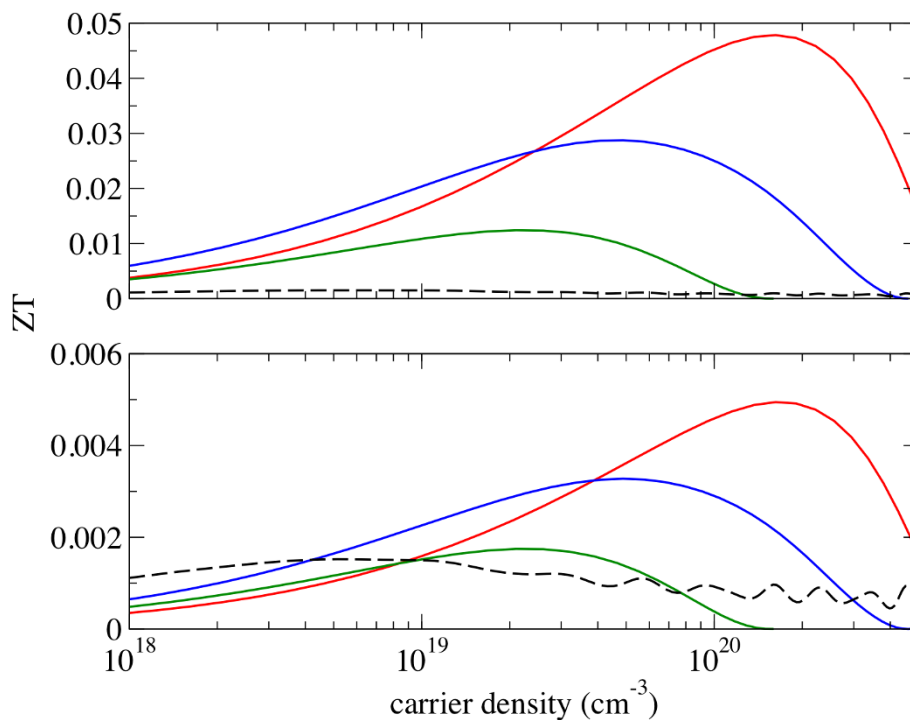


Figure 2 ZT of ZnO NWs of 8 nm (red), 10 nm (blue), and 17 nm (green) in diameter. The bulk values (black dashed lines) are shown for comparison. Top panel: The lattice contribution of thermal conductivity obtained from the molecular dynamics calculations is used. Bottom panel: The lattice contribution of thermal conductivity of bulk ZnO (85 W/Km) is used for the calculation of the NW ZT. (Color online).

Table 1 Enhancement of ZT in ZnO and Si NW

	NW diameter (Å)			
	ZnO		Si	
	8	10	17	12
$\zeta = ZT^*/ZT^*_{\text{bulk}}$	31.5	18.9	8.17	20.5
$\zeta_e = ZT^*(\kappa_l^{\text{bulk}})/ZT^*_{\text{bulk}}$	3.25	2.15	1.15	0.264
$\zeta_l = \zeta/\zeta_e$	9.69	8.79	7.10	77.7

$\zeta = ZT^*/ZT^*_{\text{bulk}}$ is the ratio of the maximum ZT of NW to maximum ZT of bulk ZnO. ζ_e and ζ_l are electronic and lattice contribution to ζ .

bulk. Nevertheless, the reduction in the lattice thermal conductivity is by almost a factor of 90 leads to the more than 70-fold lattice contribution to the enhancement of ZT. (Note that the lattice thermal conductivity of Si nanowires is highly anisotropic and very sensitive to the geometry of the surface.)

Finally, we note that the maximum values of ZT we obtain for ZnO NW is approximately 0.05 and similarly it is approximately 0.06 in Si NW. This is much smaller than the previously calculated value in Si NW, approximately 1.55 [4]. The differences between these calculations appear to arise from the differences in computed electric conductivity and consequently power factors. The values of electric conductivity for bulk Si computed here are in agreement with that of the experiment [23] for electron concentrations between 10^{17} to 10^{20} cm^{-3} as well as previous calculations (Ref. [5]), while it appears to be overestimated in Ref. [4]. The values of ZT computed here suggest that reducing the scale of nanostructures alone does not improve the ZT to a practical degree. Our findings indicate that other mechanisms

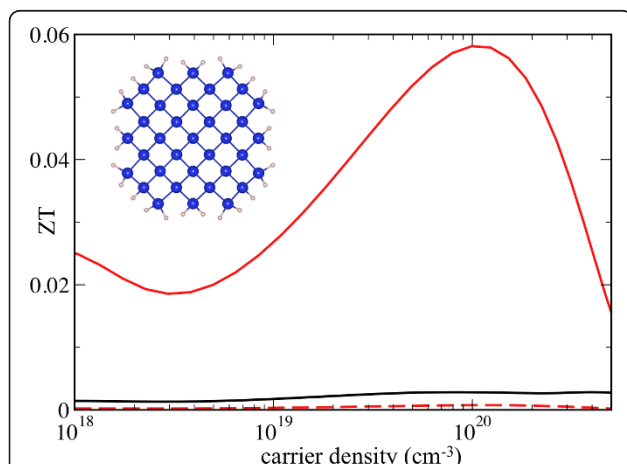


Figure 3 ZT of 12-Å diameter Si NW's (red) and bulk Si (black). The dashed (red) line is the ZT of the same Si NW calculated with bulk lattice thermal conductivity. The inset shows the cross-section atomic configuration of the NW. The NW axis direction is [001]. The lattice contributions of thermal conductivity of bulk Si and the NW, 254 and 2.8 W/Km, respectively, were derived from MD calculations. (Color online).

must be involved in the improvement of ZT, in addition to using nanocrystals. For example, in recent experiments, the enhanced ZT values in nanowires were obtained due to surface roughness and impurity scattering [33,34].

Conclusion

In conclusion, we presented the results of BTE calculations of ZnO and Si NWs based on electronic and lattice properties computed using DFT and classical MD, respectively. Not all electronic and lattice thermal coefficients change favorably when size of the nanowire is reduced. By decoupling the effects of electronic and lattice thermal conductivity on ZT values of semiconductor nanowires, we found that the reduction in κ_l plays a predominant role in the enhancement of ZT. For example, for the 8 Å ZnO and 12 Å Si nanowire, this enhancement is by a factor of 10 and 78, respectively. We conclude that for ZnO nanowires with diameter of 17 Å and larger, the lattice thermal conductivity contribution to the enhanced ZT is overwhelmingly more important than that of the electrons. Opposite to the common belief, the electronic contribution changes disadvantageously in Si NWs. In both materials, although the improvement in ZT is substantial in comparison with the bulk, the ZT of about approximately 0.05 are the maximal achievable values as a result of scaling down of the materials to the nanoscale level (down to about 10 Å).

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Authors' contributions

DOD carried out molecular dynamics calculations and some of the density functional theory (DFT) calculations. PDH and BL performed DFT calculations of the electronic part of thermal conductivity. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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