Low-temperature thermal rectification by tailoring isotope distributions

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We combine first-principles electronic structure calculated thermal conductivity data with a numerical solution of the one-dimensional heat equation to show that an asymmetric distribution of impurity scattering, if suitably designed, yields the conditions for a low-temperature thermal rectification. This happens as a result of the differences in the peaks of the temperature dependence of the thermal conductivity. We demonstrate the effectiveness of the method by probing the thermal rectification rendered by a silicon slab with a steplike position-dependent isotopic composition. The same conclusions are obtained by using experimentally measured values of the thermal conductivity of Si samples with different isotope distributions.

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I. INTRODUCTION

A thermal diode is a system whose thermal resistance depends on the sign of the applied thermal gradient and where, accordingly, heat current preferentially flows in one direction [1]. These devices are one of the key building blocks of phononics and, if good efficiencies could be achieved, would pave the way for the designing of thermal circuits that use heat to process information [2].

Early theoretical proposals [3,4] have shown that thermal rectification requires an asymmetry along the transport direction and a nonlinearity [5], a condition achieved when the thermal conductivity is a nonseparable function of the temperature and of the position [6]. A simple approach to satisfy such a necessary condition is represented by heterojunctions of materials with a different dependence of the thermal conductivity on temperature, $\kappa(T)$.

Thermal rectification is normally defined as

$$\gamma = \frac{J_{\text{fwd}} - J_{\text{rev}}}{J_{\text{rev}}} \times 100, \quad (1)$$

where J_{fwd} and J_{rev} are the heat fluxes under forward (phonons travel from right to left) and reverse (phonons travel from left to right) thermal bias, respectively. Dames [5] derived a linearized theory that, under the assumption that κ has a power-law temperature dependence and that the thermal bias is low, predicts that the maximum thermal rectification can be expressed as

$$\gamma_{\text{max}} \simeq \frac{1}{4}(n_1 - n_2)\Delta T/T_0, \quad (2)$$

where n_1, n_2 are the exponents of the $\kappa(T^n)$ curves of the two materials, $\Delta T = T_H - T_C$ is the applied thermal bias, and $T_0 = (T_H + T_C)/2$ is the mean temperature (T_H and T_C are the temperatures of the hot and cold thermal reservoirs). The effective rectification achieved, $\gamma \leq \gamma_{\text{max}}$, depends on the level of *matching* of the thermal resistances of the two materials [5,7,8], R_A and R_B , because in the limit of $R_A \gg R_B$

all the applied ΔT drops on material A and no rectification is observed (analogously when $R_B \gg R_A$).

According to Eq. (2) γ_{max} is proportional to $n_1 - n_2$ and, thus, power factors as different as possible are needed to maximize the rectification [9]. However, at temperatures larger than a few tens of Kelvin, where Umklapp processes are the dominant scattering mechanism and κ is a decreasing function of the temperature, the power factors n of most materials are rather similar [5,10]. At very low temperature, on the other hand, κ in bulk materials is dominated by impurity scattering; it increases with temperature and reaches a maximum before Umklapp processes take over. A large thermal rectification in the very low temperature regime can be in principle achieved by juxtaposing materials with $\kappa(T)$ peaks at different temperatures. In the temperature range where the thermal conductivity of one of the two materials is already dominated by Umklapp scattering, while the other is still limited by impurity scattering, n_1 and n_2 have opposite sign, the best possible scenario to yield large values of γ_{max} .

This strategy can in principle be pursued with bulk heterojunctions, but only lattice-matched materials, with defect-free interfaces, can be considered. Otherwise the interface thermal resistance—whose rectification is negligible for resistance matched materials [11]—would dominate the overall thermal resistance. Semiconducting nanowires [12,13] offer in principle a solution to overcome this limitation, because they allow releasing laterally the strain that builds up as a result of lattice mismatch [14,15]. However, the temperature independent nature of boundary scattering—a dominant scattering mechanism in thin nanowires—results in $\kappa(T)$ curves which are rather flat [16] and make this approach inefficient.

In this paper we calculate the low temperature thermal transport and propose an approach to achieve sizable rectifications based on an asymmetric distribution of the impurity scattering. As a proof of concept, we study a silicon slab in which the impurity scattering asymmetry is introduced through a position dependent steplike isotopic composition. The latter tunes the $\kappa(T)$ peak, so that it develops differently in the two regions of the material.

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FIG. 1. (a) Calculated thermal conductivity as a function of temperature of isotopically purified ²⁸Si (black circles) and natural Si (red squares). (b) Thermal conductivity of silicon single crystals along the [100] axis as a function of temperature measured by the steady-state heat flow technique with two thermometers and one heater. Data is shown for natural Si (^{nat}SiA100) and for two different levels of isotopic enrichment: ²⁸SiA100 has 99.995% of ²⁸Si, 0.0046% of ²⁹Si, and 0.0004% of ³⁰Si, while ²⁸SiB100 has 99.92% of ²⁸Si, 0.075% of ²⁹Si, and 0.005% of ³⁰Si. Reprinted with permission from Ref. [31], copyright 2018 The American Institute of Physics.

II. COMPUTATIONAL METHODS

At first we calculate the second- and third-order interatomic force constants (IFCs) from finite differences [17] within density-functional theory (DFT) using the QUANTUM ESPRESSO package [18]. We used the local density approximation (LDA) [19] for the exchange-correlation energy and a plane-wave cutoff of 1600 eV with norm-conserving pseudopotentials. We optimized the cell lattice parameter until the stress was lower than 0.01 kbar and verified that the forces on the atoms were lower than 10^{-11} eV/Å; because of the great accuracy needed in the calculation of the atomic forces we iterate the electronic self-consistency loop until changes in the total energy and eigenvalues become lower than 10^{-11} eV.

Then we used the IFCs to solve the linearized Boltzmann transport equation (BTE) for phonons using the kinetic-collective approach [20], where finite size effects can be included through Casimir's expression [21] for boundary scattering ($\Gamma_B = v/(2\pi L)$), where v is the group velocity and L the characteristic size of the sample. The ALAMODE code [22] is used to calculate harmonic and anharmonic properties in a $160 \times 160 \times 160$ and $40 \times 40 \times 40$ $\mathbf{q}$ -point grid, respectively. Calculating $\kappa(T)$ at very low temperatures, where heat transport is dominated by long wavelength phonons and where the BTE should be solved on a very high density mesh in $\mathbf{q}$ space, is a formidable computational task, unless very large boundary scattering terms (i.e., corresponding to submicrometer size) are included. To circumvent this problem and to ensure the convergence of $\kappa(T)$ even at very low temperatures, we use the analytic expressions from Herring [23] and Han and Klemens [24] to extrapolate the anharmonic properties (i.e., the phonon-phonon scattering rates) up to a $160 \times 160 \times 160$ $\mathbf{q}$ -point grid. The convergence and agreement of $\kappa(T)$ with the experimental data below 10 K is ensured through the inclusion of a boundary scattering of 2.8 mm [25]. We use this approach to calculate the thermal conductivity $\kappa(T)$ of

different isotope compositions. To this end, we employ the model proposed by Tamura [26] to account for mass-defect scattering.

Once the $\kappa(T)$ of two given isotope blends are known we solve the one-dimensional stationary heat equation

$$\frac{\partial}{\partial z} \left[\kappa(z) \frac{\partial T(z)}{\partial z} \right] = 0 \quad (3)$$

to find the temperature profile $T(z)$ for a given thermal bias, ΔT . The overall thermal resistance is then easily calculated as

$$R_{\text{tot}} = \int_0^{L_A} \frac{1}{S_A} \kappa_A^{-1}[T(z)] dz + \int_{L_A}^{L_A+L_B} \frac{1}{S_B} \kappa_B^{-1}[T(z)] dz, \quad (4)$$

where $S_{A,B}$, $L_{A,B}$, and $\kappa_{A,B}$ are the cross section, the length, and the temperature dependent conductivity of materials A and B . The thermal rectification is computed by solving the heat equation for pairs of thermal bias $\pm \Delta T$ and comparing the heat fluxes, $J \propto R_{\text{tot}}^{-1}$ [see Eq. (1)].

Notice that the scheme for rectification that we discuss requires a diffusive regime for heat transport. Available experimental data [27–29] indicate that this condition is fulfilled by samples of millimetric size—say 2–3 mm—being the characteristic mean free path of Si, even at temperatures as low as 10 K, of the order of 2–300 μm . For this reason we use a boundary scattering term corresponding to a sample size of ~ 3 mm and we can neglect the thermal resistance of the interface [30] in Eq. (4).

III. RESULTS AND DISCUSSION

At first we consider a junction between a left region of isotopically purified Si, where almost all the atoms are ²⁸Si (in practice we consider a purity of 99.99%), and a right region

FIG. 2. Thermal rectification as a function of $T_0 = (T_H + T_C)/2$ of a junction made of a segment of length L_A of isotopically purified ^{28}Si and a segment of length L_B of natural Si, for different values of $\Phi = L_A/(L_A + L_B)$ and a thermal bias $\Delta T = T_H - T_C$ of (a) 10 K and (b) 30 K.

of natural Si, where the relative abundance of isotopes is the one found in nature, i.e., $^{28}\text{Si}_{0.922}$, $^{29}\text{Si}_{0.047}$, and $^{30}\text{Si}_{0.031}$. The $\kappa(T)$ of these two materials are displayed in Fig. 1(a). As the temperature approaches to zero, anharmonic scattering becomes negligible, until the thermal conductivity is only limited by boundary and impurity scattering. In high purity materials, where point defects such as vacancies, interstitials, and antisites are absent, such a scattering derives from isotopes, which are the only responsible of the low-temperature finite value of κ . Therefore isotope purified materials—where one single isotope is present—that have no intrinsic or extrinsic defects have a divergent thermal conductivity at $T \rightarrow 0$ approaching the ballistic regime. In practice the experimental thermal conductivity is limited by the boundary scattering due to the finite size of the sample. The peak that we obtain at ~ 22 K (later on referred to as $T_{\kappa_{28}\text{Si},\text{max}}$) is due to a residual isotope scattering—the system is only 99.99% pure ^{28}Si —needed to avoid numerical divergence and to boundary scattering. Natural Si, on the other hand, features a peak at 28 K.

As a result of the absence of an efficient scattering mechanism at very low temperatures, the thermal conductivity of the isotopically purified sample is significantly larger than the one of natural Si. As discussed above, the thermal resistance of the two segments should be of the same order. If this resistance-matching condition is not met the thermal rectification deriving from the bulk properties of the two materials is suppressed because almost all the applied thermal bias drops on one of them. Therefore, we compute the thermal rectification, γ , for different T_0 , different $|\Delta T|$, but also for different $\Phi = L_A/(L_A + L_B)$, where L_A (L_B) is the length of the less (more) resistive material, in order to have an insight on the best resistance-matching condition.

Our results, for $\Delta T = 10$ and 30 K and as a function of T_0 are shown in Fig. 2 for four different values of Φ . As can be seen there, rectifications γ of the order of -25 to 15% are obtained for $\Delta T = 10$ K. These rectification values exceed by almost one order of magnitude the rectification obtained experimentally by Chang *et al.* [32] in asymmetrically mass-loaded nanotubes and are similar to those of the junction between two cobalt oxides reported by Kobayashi [33]. Increasing ΔT to 30 K leads to thermal rectifications

FIG. 3. Thermal rectification as a function of T_0 for $\Phi = 0.8$ and $\Delta T = 10$ (a) and 30 K (b). We consider different degrees of purity of the isotopically purified side of the junction; we also include a combination of isotopically purified Si and a Si segment with a higher degree of isotopical disorder than natural Si.

that reach values as large as 40% at $T_0 \sim 35$ K. In both ΔT configurations, a reversal of the preferential transport direction occurs at $T_0 \sim T_{\kappa_{28}\text{Si},\text{max}}$, which demonstrates that this is an effect directly related to the change of slope sign in the $\kappa(T)$ of the isotopically purified region. Notice that due to the large mismatch in the thermal conductivity illustrated in Fig. 1(a), large values of Φ are necessary to attain the resistance matching regime.

These large rectification factors, however, are subordinated to the possibility of obtaining highly isotopically purified Si, where *almost all* the atoms have the same mass, ^{28}Si in our case. In order to study the dependence of γ on the level of isotopical purity, we have considered thermal diodes in which natural Si is combined with $^{28}\text{Si}_{0.99}$ and $^{28}\text{Si}_{0.995}$ (the remaining molar fractions being equally completed with ^{29}Si and ^{30}Si). Figure 3 displays the rectification obtained for a fixed $\Phi = 0.8$. The rectifications are now smaller, as expected, but have peak values that are still considerably high and range between $\pm 15\%$, depending on the thermal bias condition and on the composition of the isotopically purified part of the junction. In Fig. 3 we have also included a junction of isotopically purified Si and a Si segment with a higher degree of isotopical disorder than natural Si. This result highlights how the rectification can also be tuned, although to a lesser degree, by introducing additional disorder on one side of the

FIG. 4. Thermal rectification for $T_0 = 10$ K and $\Delta T = 10$ (a) and 30 K (b) as a function of Φ for junctions of Si segments with different degrees of isotopical purity.

FIG. 5. Thermal rectification as a function of T_0 for a junction made of a segment of $^{28}\text{SiA100}$ and a segment of $^{\text{nat}}\text{SiA100}$, as defined above, for different values of Φ and a thermal bias $\Delta T = T_H - T_C$ of 10 K (a) and 30 K (b).

junction and not only by isotopical purification of the other side.

As the content of ^{29}Si and ^{30}Si increases, the conductivity mismatch with natural Si decreases and the matching condition of the thermal resistance is met for lower Φ s, i.e., less dissimilar L_A and L_B . This is illustrated in Fig. 4, where we have plotted the thermal rectification at $T_0 = 10$ for $\Delta T = 10$ and 30 K as function of Φ for the four systems previously studied. Besides observing that higher isotope purity results in larger thermal rectification, one can also see that the value of Φ that maximizes $|\gamma|$ becomes smaller as the mismatch between the isotopic concentrations is reduced.

Calculating the thermal conductivity at very low temperature is a delicate task. In order to prove that within the scheme here described large rectifications could indeed be observed and they do not depend critically on the computed values of $\kappa(T)$, we have used as input for Eqs. 3-1 the recent experimental results of Inyushkin *et al.* [31], who measured the thermal conductivity of isotopically enriched silicon with different degrees of purity [see Fig. 1(b)]. In this way we solve the one-dimensional stationary heat equation and estimate the thermal rectification as we did above, but this time we rely on values of the thermal conductivity as a

function of temperature obtained experimentally, rather than calculated. The results, shown in Figs. 5(a) and 5(b), indicate that sizable thermal rectifications can still be obtained, with values of up to the 40% for $\Delta T = 30$ K. The agreement with the results based on the computed $\kappa(T)$ shown in Fig. 2 is remarkable both on the qualitative and quantitative viewpoint, stressing the robustness of the results discussed thus far and witnessing the accuracy of the theoretical predictions [34,35].

IV. CONCLUSIONS

In summary, we have shown that large thermal rectifications can be obtained in the low temperature regime with a position dependent isotope composition. Controlling the isotope composition allows tuning the peaks of the temperature dependence of the thermal conductivity, which determines the heat rectification. We have separately discussed the effect of the isotopical purity needed to observe sizable effects. We observe, however, that implementations of these concepts in a realistic device will have to take into account the thermal contact resistance with the heat baths [36,37], as large values may easily mask the predicted rectifying behavior. As a final remark, it is worth noticing the universality of the proposed thermal rectification mechanism which is applicable to any material as long as its isotopical purity can be engineered. Besides, aside from the isotopic distribution, other types of pointlike defects can be used to asymmetrically modulate the phonon scattering in the low temperature regime, likely producing the same effect.

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- [1] C. Starr, *Physics* **7**, 15 (1936).
 - [2] N. Li, J. Ren, L. Wang, G. Zhang, P. Hänggi, and B. Li, *Rev. Mod. Phys.* **84**, 1045 (2012).
 - [3] M. Terraneo, M. Peyrard, and G. Casati, *Phys. Rev. Lett.* **88**, 094302 (2002).
 - [4] B. Li, L. Wang, and G. Casati, *Phys. Rev. Lett.* **93**, 184301 (2004).
 - [5] C. Dames, *J. Heat Transfer* **131**, 061301 (2009).
 - [6] M. Peyrard, *Europhys. Lett.* **76**, 49 (2006).
 - [7] M. López-Suárez, M. Royo, and R. Rurali, *Phys. Rev. Mater.* **2**, 113001 (2018).
 - [8] M. López-Suárez, I. Neri, and R. Rurali, *J. Appl. Phys.* **124**, 224301 (2018).
 - [9] T.-M. Shih, Z. Gao, Z. Guo, H. Merlitz, P. J. Pagni, and Z. Chen, *Sci. Rep.* **5**, 12677 (2015).
 - [10] Y. S. Touloukian, R. W. Powell, C. Y. Ho, and P. G. Klemens, *Thermophysical Properties of Matter - The TPRC Data Series. Volume 2. Thermal Conductivity - Nonmetallic Solids* (IFI/Plenum, New York, 1970).
 - [11] R. Rurali, L. Colombo, X. Cartoixa, O. Wilhelmsen, T. T. Trinh, D. Bedeaux, and S. Kjelstrup, *Phys. Chem. Chem. Phys.* **18**, 13741 (2016).
 - [12] W. Lu and C. M. Lieber, *J. Phys. D: Appl. Phys.* **39**, R387 (2006).
 - [13] R. Rurali, *Rev. Mod. Phys.* **82**, 427 (2010).
 - [14] M. Amato, M. Palummo, R. Rurali, and S. Ossicini, *Chem. Rev.* **114**, 1371 (2014).
 - [15] M. Royo, M. D. Luca, R. Rurali, and I. Zardo, *J. Phys. D: Appl. Phys.* **50**, 143001 (2017).
 - [16] D. Li, Y. Wu, P. Kim, L. Shi, P. Yang, and A. Majumdar, *Appl. Phys. Lett.* **83**, 2934 (2003).
 - [17] K. Esfarjani and H. T. Stokes, *Phys. Rev. B* **77**, 144112 (2008).
 - [18] P. Giannozzi *et al.*, *J. Phys.: Condens. Matter* **21**, 395502 (2009).

- [19] D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- [20] P. Torres, A. Torelló, J. Bafaluy, J. Camacho, X. Cartoixa, and F. X. Alvarez, *Phys. Rev. B* **95**, 165407 (2017).
- [21] H. Casimir, *Physica* **5**, 495 (1938).
- [22] T. Tadano, Y. Gohda, and S. Tsuneyuki, *J. Phys.: Condens. Matter* **26**, 225402 (2014).
- [23] C. Herring, *Phys. Rev.* **95**, 954 (1954).
- [24] Y.-J. Han and P. G. Klemens, *Phys. Rev. B* **48**, 6033 (1993).
- [25] P. Torres, *Thermal Transport in Semiconductors: First Principles and Phonon Hydrodynamics* (Springer Nature, Switzerland, 2018).
- [26] S. i. Tamura, *Phys. Rev. B* **27**, 858 (1983).
- [27] R. Gereth and K. Hubner, *Phys. Rev.* **134**, A235 (1964).
- [28] L. Weber and E. Gmelin, *Appl. Phys. A* **53**, 136 (1991).
- [29] O. Bourgeois, D. Tainoff, A. Tavakoli, Y. Liu, C. Blanc, M. Boukhari, A. Barski, and E. Hadji, *C. R. Phys.* **17**, 1154 (2016).
- [30] E. T. Swartz and R. O. Pohl, *Rev. Mod. Phys.* **61**, 605 (1989).
- [31] A. V. Inyushkin, A. N. Taldenkov, J. W. Ager, E. E. Haller, H. Riemann, N. V. Abrosimov, H.-J. Pohl, and P. Becker, *J. Appl. Phys.* **123**, 095112 (2018).
- [32] C. W. Chang, D. Okawa, A. Majumdar, and A. Zettl, *Science* **314**, 1121 (2006).
- [33] W. Kobayashi, Y. Teraoka, and I. Terasaki, *Appl. Phys. Lett.* **95**, 171905 (2009).
- [34] D. A. Broido, M. Malorny, G. Birner, N. Mingo, and D. A. Stewart, *Appl. Phys. Lett.* **91**, 231922 (2007).
- [35] A. Ward, D. A. Broido, D. A. Stewart, and G. Deinzer, *Phys. Rev. B* **80**, 125203 (2009).
- [36] S. Yazji, E. A. Hoffman, D. Ercolani, F. Rossella, A. Pitanti, A. Cavalli, S. Roddaro, G. Abstreiter, L. Sorba, and I. Zardo, *Nano Res.* **8**, 4048 (2015).
- [37] S. Yazji, M. Y. Swinkels, M. D. Luca, E. A. Hoffmann, D. Ercolani, S. Roddaro, G. Abstreiter, L. Sorba, E. P. A. M. Bakkers, and I. Zardo, *Semicond. Sci. Technol.* **31**, 064001 (2016).