

Electric control of the heat flux through electrophononic effects

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(Dated: May 23, 2018)

We demonstrate a fully electric control of the heat flux, which can be continuously modulated by an externally applied electric field in PbTiO₃, a prototypical ferroelectric perovskite, revealing the mechanisms by which experimentally accessible fields can be used to tune the thermal conductivity by as much as 50% at room temperature.

Our current ability to control heat transport in insulators is rather limited and mostly consists in modulating the amount of scattering experienced by the heat carrying phonons¹. This approach is normally pursued by designing systems with tailor-made boundaries^{2,3}, defect distributions^{4,5}, or periodical sequences of different materials or nanostructuring^{6–8}, as in superlattices and phononic crystals. These strategies allow targeting a given thermal conductivity, which can sometimes result in some degree of thermal rectification^{9–13}. Nevertheless, alternative approaches enabling a *dynamical* modulation of the thermal conductivity are seldom tackled because of the subtleties related with phonon manipulation.

The intrinsic difficulty in manipulating phonons is often ascribed to the fact that they do not possess a net charge or a mass; thus, it is difficult to control their propagation by means of external fields¹⁴. However, this is not always the case^{15–18}. Insulators or semiconductors often feature polar phonons –which typically involve atoms with different charges, and have a vibrating electric dipole associated to them– that can be acted upon by an external electric field, to *harden* or *soften* them, which should result in a modulation of the thermal conductivity. Further, the structural dielectric response of an insulator, which is mediated by these very polar modes, may have significant effects in the entire phonon spectrum, via anharmonic couplings, and further affect the conductivity. Here we exploit this simple, yet almost unexplored, idea. We show that the thermal conductivity can indeed be controlled by an external applied electric field, and that this effect leads to a genuine thermal counterpart of the field effect in usual electronic transistors. Indications that such an electrophononic effect can be obtained experimentally have been previously reported in SrTiO₃ at very low temperatures^{19,20}

We consider PbTiO₃ (PTO), a ferroelectric (FE) perovskite that below a Curie temperature $T_C \approx 760$ K has a spontaneous electric polarization \mathbf{P} associated to the off-centering of the cations with respect to the surrounding oxygen atoms^{21,22}. PTO's FE phase is tetragonal, with $\mathbf{P} = P_z(0, 0, 1)$ lying along one of the (pseudo)cubic directions of the perovskite lattice, as sketched in Figure 1. By applying electric fields above the so-called coercive field E_{coe} (which typically lies in the 10^6 – 10^7 V/cm range), it is possible to reverse such a polar distortion, even in small (nanometric) regions, so that FE domains

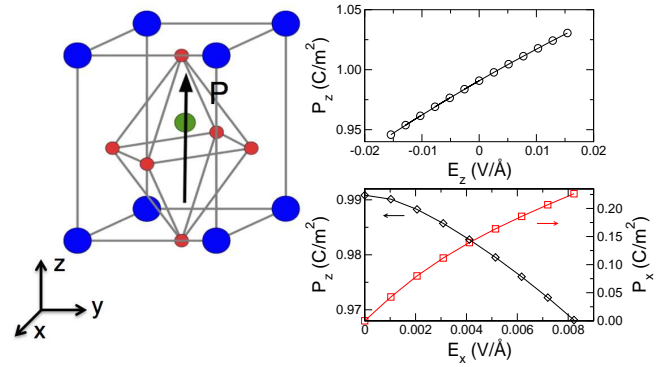


FIG. 1. (Left) Sketch of a PbTiO₃ unit cell. Pb, Ti, and O atoms are represented by blue, green, and red spheres, respectively. (Right) Polarization as a function of a parallel/antiparallel electric field, E_z and of a perpendicular field, E_x ; in the latter case we display both P_x and P_z , whose increase/decrease allows appreciating the rotation of \mathbf{P} .

can be written. Interestingly, recent works show that juxtaposed domains with different orientations of \mathbf{P} can be used as phonon switches²³ and phonon polarizers²⁴. Here we consider $E < E_{\text{coe}}$, exploiting the fact that, like most FE materials, PTO displays a rather large structural (dielectric) response to even moderate applied fields.

All our simulations of PTO are carried out within second-principles density-functional theory (SPDFT) as implemented in the SCALE-UP code^{25,26}. SPDFT has a demonstrated predictive power for the key structural, vibrational and response properties of FE perovskite oxides^{27–31}. Further, as most first-principles approaches, SPDFT reproduces accurately the vibrational and response properties of PTO²⁵, which are closely related to the quantities discussed here; hence, we expect our results to be quantitatively accurate. For more details on the used SPDFT methods and the technicalities of our calculations, please see the Supplemental Material (SM)³². We also observe that, although our simulations are based on a model constructed to reproduce the behavior of bulk PbTiO₃, previous studies showed that the same model works well in a variety of conditions that differ from those considered to compute its parameters. This has been amply demonstrated, thanks e.g. to the application of the same PbTiO₃ model employed in this study, in a variety of investigations of

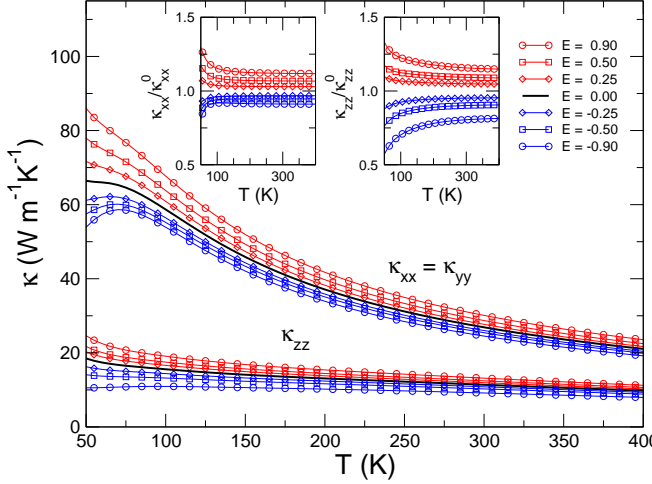


FIG. 2. Thermal conductivity as a function of temperature for different values of the parallel ($E_z > 0$) and antiparallel ($E_z < 0$) electric field. The inset shows the relative change of the thermal conductivity as the ratio of its value with and without external field, $\kappa_{xx}/\kappa_{xx}^0$ (left) and $\kappa_{zz}/\kappa_{zz}^0$ (right). Fields are given in unit of the parallel coercive field, $E_{\text{coe},z}$

PbTiO₃/SrTiO₃ superlattices^{30,31,33}, which include successful comparisons with first-principles calculations and literature³⁴ as well as with experiment. Hence, the employed models are *transferable* to treat the most common thin film and superlattice geometries.

For the calculation of the thermal conductivity tensor, we proceed as follows. For each applied field, we first relax the structure by means of a Monte Carlo simulated annealing, automatically accounting for all dielectric and piezoelectric effects that may impact the thermal conductivity³⁵. Then, we calculate the second-order interatomic force constants (IFCs) by finite differences in a $8 \times 8 \times 8$ supercell³⁶. We use the same supercell to compute third-order IFCs³⁷, considering interactions up fourth (twelfth) nearest-neighbors for parallel (perpendicular) fields, which we check provides good convergence. We then use the IFCs to calculate the anharmonic scattering rates and solve numerically the linearized Boltzmann Transport Equation (BTE), employing the iterative method implemented in the ShengBTE code³⁷ on a $8 \times 8 \times 8$ \mathbf{q} -point grid. Scattering from isotopic disorder is accounted for within the model of Tamura³⁸.

The lattice thermal conductivity is then obtained as

$$\kappa_{ij} = \sum_{\lambda} \kappa_{ij,\lambda} = C \sum_{\lambda} f_{\lambda}(f_{\lambda} + 1)(h\nu_{\lambda})^2 v_{i,\lambda} F_{j,\lambda}, \quad (1)$$

where i and j are the spatial directions x , y , and z . $C^{-1} = k_B T^2 \Omega N$, where k_B , h , T , Ω and N are, respectively, Boltzmann's constant, Planck's constant, the temperature, the volume of the 5-atom unit cell, and the number of \mathbf{q} -points. The sum runs over all phonon modes, the index λ including both \mathbf{q} -point and phonon band. f_{λ} is the equilibrium Bose-Einstein distribution function, and ν_{λ} and $v_{i,\lambda}$ are, respectively, the frequency and group velocity of phonon λ . The mean free displace-

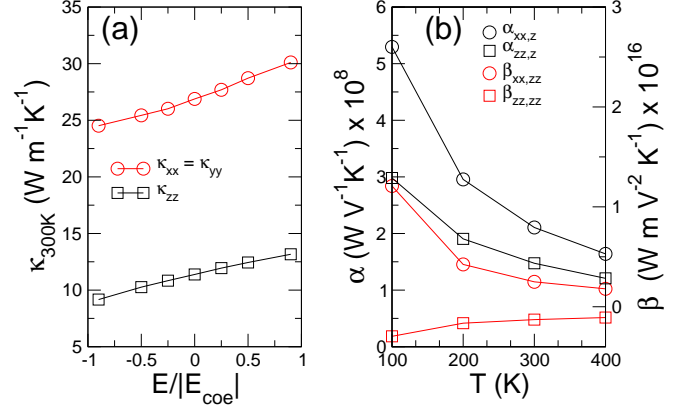


FIG. 3. (a) Dependence on the electric field, E_z , of the room temperature thermal conductivity. (b) Coefficients α and β of Eq. 2 as a function of temperature for fields applied parallel to the \mathbf{P} vector.

ment $F_{j,\lambda}$ is initially taken to be equal to $\tau_{\lambda} v_{j,\lambda}$, where τ_{λ} is the lifetime of mode λ within the relaxation time approximation (RTA). Starting from this guess, the solution is then obtained iteratively and $F_{j,\lambda}$ takes the general form $\tau_{\lambda}(v_{j,\lambda} + \Delta_{j,\lambda})$, where the correction Δ_{λ} captures the changes in the heat current associated to the deviations in the phonon populations computed at the RTA level^{39,40}.

Our calculations thus yield κ_{ij} as a function of applied field and temperature, and we fit our results to

$$\kappa_{ij}(T, \mathbf{E}) = \kappa_{ij}^0(T) + \sum_k \alpha_{ij,k}(T) E_k + \sum_{kl} \beta_{ij,kl}(T) E_k E_l, \quad (2)$$

where we introduce the thermal-response tensors α and β , κ^0 being the conductivity at zero field. Note that, because of the high tetragonal symmetry of PTO's FE phase ($P4mm$ space group), the number of independent tensor components in Eq. (2) is small. For example, we have $\kappa_{ij}^0 = \delta_{ij} \kappa_{ii}^0$, and $\kappa_{xx}^0 = \kappa_{yy}^0 \neq \kappa_{zz}^0$. Here we focus on the behavior of κ_{xx} , κ_{yy} , and κ_{zz} as a function of fields parallel (along z) and perpendicular (along x) to P_z . We thus calculate $\alpha_{xx,z} = \alpha_{yy,z}$ and $\alpha_{zz,z}$, noting that $\alpha_{ii,x} = \alpha_{ii,y} = 0$ by symmetry; and we also calculate $\beta_{xx,xx}$, $\beta_{yy,xx}$, and $\beta_{zz,xx}$, as well as $\beta_{xx,zz} = \beta_{yy,zz}$ and $\beta_{zz,zz}$.

To explore the linear and non-linear responses, we consider field values in a range up to 90% of the theoretical E_{coe} . Working with an idealized monodomain PTO state with $P_z > 0$, our predicted coercive fields are $E_{\text{coe},z} \approx -1.5 \cdot 10^8$ V/m (to reverse P_z to $-P_z$) and $E_{\text{coe},x} \approx 8.2 \cdot 10^7$ V/m (to rotate from P_z to P_x , a symmetry-equivalent x -polarized FE phase). These fields are relatively large when compared with experimental values, an issue that is typical of first-principles works on FE switching⁴¹ and which is probably related, e.g., to the absence of nucleation centers for the polarization reversal (defects, interfaces) in the simulations. This matter is not important here. Incidentally, note that it is customary to apply fields as large as these ones to FE

thin films, using voltages of a few hundreds meV.

Let us discuss first the response to fields $\mathbf{E} = E_z(0, 0, 1)$, which can be parallel ($E_z > 0$) or antiparallel ($E_z < 0$) to the electric polarization $P_z > 0$ (see the SM for the hysteretic response). Figure 2 shows the thermal conductivity components κ_{xx} and κ_{zz} , as a function of temperature, for several values of E_z . Let us first note that the zero-field conductivities feature a considerable anisotropy, with, e.g., $\kappa_{xx}^0 = 26.9 \text{ W m}^{-1}\text{K}^{-1}$ and $\kappa_{zz}^0 = 11.4 \text{ W m}^{-1}\text{K}^{-1}$ at room temperature (T_{room}). This is a direct consequence of the FE distortion along z , and suggests that, if the electric field is able to affect the polarization considerably, it will also have a significant effect in the conductivity. This is indeed what we find. As shown in Figure 2, parallel fields yield an increase of both κ_{xx} and κ_{zz} , while antiparallel fields cause a decrease. To better appreciate this effect we plot the relative variation of the thermal conductivities, $\kappa_{xx}/\kappa_{xx}^0$ and $\kappa_{zz}/\kappa_{zz}^0$ in the inset.

Further insight can be gathered from Figure 3a, which shows the variation of both κ components as a function of E_z at T_{room} . The obtained smooth behavior can be easily fitted using the quadratic expression in Eq. (2), and Figure 3b shows the T -dependence of the corresponding α and β coefficients. The linear response clearly dominates, with room-temperature values of $\alpha_{zz,z} = 1.47 \cdot 10^{-8} \text{ W V}^{-1}\text{K}^{-1}$ and $\alpha_{xx,z} = 2.11 \cdot 10^{-8} \text{ W V}^{-1}\text{K}^{-1}$. As regards the magnitude of the effect, for $E_z = 0.5 \times E_{\text{coe},z}$ at T_{room} we obtain changes of about 7% and 9% in κ_{xx} and κ_{zz} , respectively. These large effects are ultimately a consequence of PTO's considerable structural response to the applied fields, as evidenced by the variation of P_z shown in Figure 1. The corresponding lattice contribution to the dielectric susceptibility is about 31.

To gain further insight into these results, we find it convenient to analyze Eq. (1) in the following way. First, we group all the terms that are explicitly dependent on the phonon frequencies by introducing $\theta_\lambda = f_\lambda(f_\lambda + 1)(h\nu_\lambda)^2$, and write the field-induced change of κ_{ij} as

$$\begin{aligned} \Delta\kappa_{ij} &= \kappa_{ij} - \kappa_{ij}^0 = \sum_{\lambda} \Delta\kappa_{ij,\lambda} \\ &= C \sum_{\lambda} [\Delta\theta_\lambda v_{i,\lambda}^0 F_{j,\lambda}^0 + \theta_\lambda^0 \Delta v_{i,\lambda} F_{j,\lambda}^0] \\ &\quad + \theta_\lambda^0 v_{i,\lambda}^0 \Delta F_{j,\lambda} + \mathcal{R}_{ij,\lambda}, \end{aligned} \quad (3)$$

where the superscript ‘‘0’’ indicates zero-field quantities, with $\Delta g = g - g^0$ for any magnitude g . This expression allows us to readily identify changes that are dominated by only one of the factors $(\theta_\lambda, v_{i,\lambda}, F_{j,\lambda})$ entering the mode conductivity, while $\mathcal{R}_{ij,\lambda}$ captures any lingering changes. (In the limit of small applied fields $\mathcal{R}_{ij,\lambda} \rightarrow 0$.) Further, we can group the changes in the mode conductivities in energy intervals, using the zero-field frequencies to assign specific modes to specific intervals, and thus plot Figure 4 to analyze the E_z -induced changes in κ_{xx} and κ_{zz} .

Two important observations can be drawn from this figure. On the one hand, the change of κ_{xx} and κ_{yy} does not depend on a particular group of phonons. Rather,

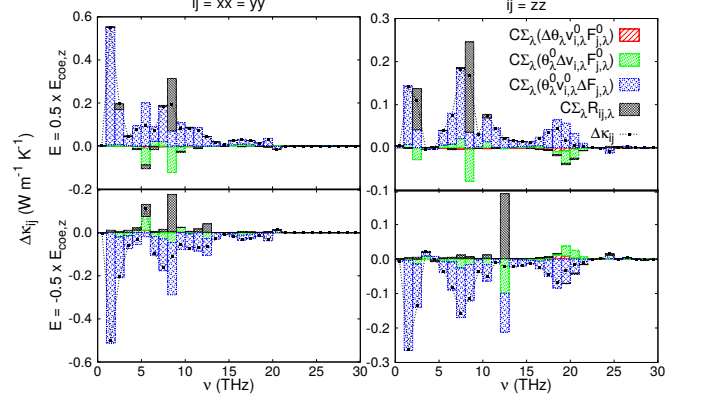


FIG. 4. The different terms of Eq. 3 in the case of a parallel field, $E_z = 0.5 \times E_{\text{coe},z}$ (upper row) and of an antiparallel field, $E_z = -0.5 \times E_{\text{coe},z}$ (bottom row). The dots indicate the variation of the total contribution to the thermal conductivity in a given frequency interval, i.e. $\Delta\kappa_{ij}$ in Eq. 3.

the complete spectrum contributes to it, in a way that is rather homogeneous. Thus, for example, we have $\Delta\kappa_{zz} > 0$ for $E_z > 0$, where the total positive change is the result of a majority of phonons having positive $\Delta\kappa_{zz,\lambda} > 0$ contributions. (Also, note the approximate symmetry of the results for $+E_z$ and $-E_z$, which is consistent with the dominant linear effect.) On the other hand, for most of the phonon spectrum, it is the change in mean free displacements that dominates the variation of the conductivity.

We can better understand the changes in $F_{j,\lambda}$ as follows. First, we can simplify our discussion by noting that $F_{j,\lambda} = \tau_\lambda(v_{j,\lambda} + \Delta_{j,\lambda}) \approx \tau_\lambda v_{j,\lambda}$, as we observe that the correction to the RTA is small, typically below a 10%. Then, we find that the changes in phonon lifetimes dominate over the variations of the group velocities, which is consistent with the relatively modest impact of the $\Delta v_{j,\lambda}$ term shown in Figure 4. Further, as described in the SM and Ref. 37, we have $\tau_\lambda^{-1} \sim f_{\lambda'} \times (\nu_\lambda \nu_{\lambda'} \nu_{\lambda''})^{-1}$, where λ' and λ'' label modes that interact with λ via a three-phonon scattering process. Hence, for example, if most phonons were to harden under application of a field $E_z > 0$, the phonon frequencies $\{\nu_\lambda\}$ would generally increase and the populations $\{f_\lambda\}$ decrease, which would yield an increase of the lifetimes $\{\tau_\lambda\}$. This is precisely what we have in our calculations, as the average phonon frequency changes from $\bar{\nu}^0 = 9.96 \text{ THz}$ to $\bar{\nu} = 10.05 \text{ THz}$ for $E_z = 0.5 \times E_{\text{coe},z}$, resulting in generally longer lifetimes and larger thermal conductivity. In contrast, for $E_z = -0.5 \times E_{\text{coe},z}$ we obtain $\bar{\nu} = 9.87 \text{ THz}$, with generally shorter lifetimes and greater thermal resistance⁴². Indeed, we find that this is the dominant effect explaining our results for κ_{xx} and κ_{zz} under fields that are (anti)parallel to the polarization P_z .

The fact that most of PTO's phonon bands become harder for $E_z > 0$ (softer for $E_z < 0$) may seem surprising at first; yet, we believe it can be rationalized as follows. According to our simulations, the application of a parallel field has two main effects. On one hand, the cell volume

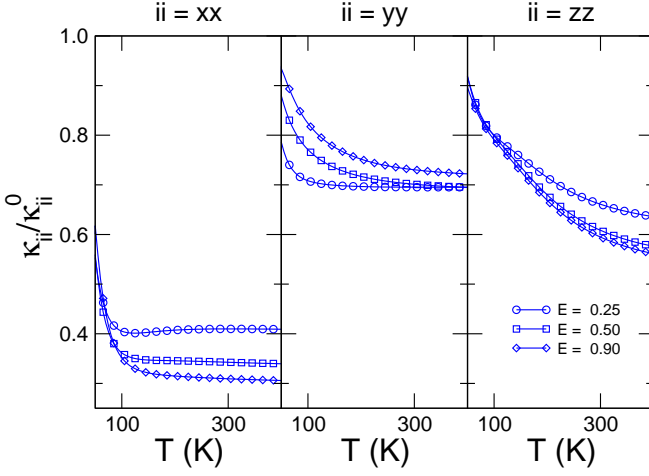


FIG. 5. Ratio of the thermal conductivity with and without a perpendicular external field, $\kappa_{xx}/\kappa_{xx}^0$ (left), $\kappa_{yy}/\kappa_{yy}^0$ (center), and $\kappa_{zz}/\kappa_{zz}^0$ (right), as a function of temperature.

grows moderately. For example, we get $\Omega/\Omega^0 = 1.0018$ for $E_z = 0.5 \times E_{\text{coe},z}$, which is a consequence of a dominant piezoelectric effect. The increased volume alone should result in a general softening (reduction) of the phonon frequencies, which is the usual behavior corresponding to a positive Grüneisen parameter. On the other hand, P_z grows for $E_z > 0$, and the stronger polar distortion can also be expected to have an impact on the phonon frequencies. More precisely, in the field of phase transitions in perovskites, it is generally observed that different distortions of the cubic perovskite structure tend to *compete* with each other, implying that the condensation of one (e.g., the polar distortion) tends to *harden* the others, thus increasing the associated phonon frequencies. (See Ref. 25 and 43) Our results suggest that this effect is dominant in PTO.

Since we attribute the changes in conductivity under E_z -field to a general hardening/softening of the phonon spectrum, it may seem strange to note in Figure 4 that the changes associated to the $\Delta\theta_\lambda$ term [Eq. (3)] are negligible (in fact, they are barely visible in the figure). Yet, note that, in this term, the variations of frequencies and populations tend to cancel each other, yielding a relatively small net effect.

Let us now move to the case in which we apply a field $\mathbf{E} = E_x(1, 0, 0)$, perpendicular to the polarization, P_z . We consider $E_x > 0$, noting that this situation is equivalent by symmetry to the application of $E_x < 0$ or fields along y . Figure 5 summarizes our results, which feature a very large decrease of all the tensor components. Thus, for example, for $E_x = 0.25 \times E_{\text{coe},x}$ at T_{room} , we get $\kappa_{xx}/\kappa_{xx}^0 = 0.41$, $\kappa_{yy}/\kappa_{yy}^0 = 0.70$, and $\kappa_{zz}/\kappa_{zz}^0 = 0.66$. This dramatic enhancement of the thermal resistance translates into very large values of the quadratic response β , as we obtain $\beta_{xx,xx} = -1.39 \cdot 10^{-12} \text{ WmV}^{-2}\text{K}^{-1}$, $\beta_{yy,xx} = -2.26 \cdot 10^{-13} \text{ WmV}^{-2}\text{K}^{-1}$, and $\beta_{zz,xx} = -6.51 \cdot 10^{-14} \text{ WmV}^{-2}\text{K}^{-1}$ at T_{room} .

Figure 6 shows the analysis based on Eq. (3), applied

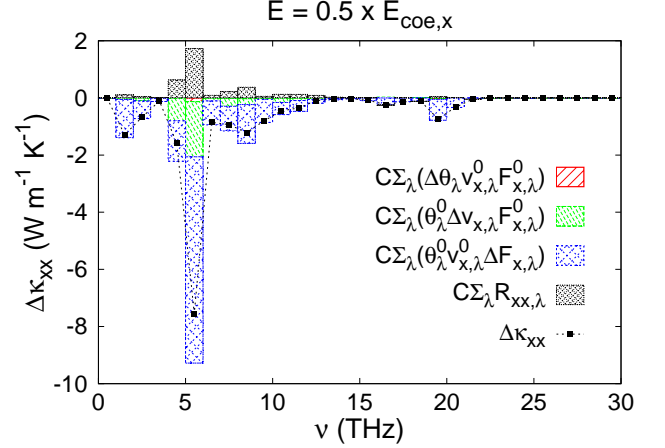


FIG. 6. The different terms of Eq. 3 in the case of a perpendicular field, $E_x = 0.5 \times E_{\text{coe},x}$. The dots indicate the variation of the total contribution to the thermal conductivity in a given frequency interval, i.e. $\Delta\kappa_{xx}$ in Eq. 3.

to the change in κ_{xx} at T_{room} for a field $E_x = 0.5 \times E_{\text{coe},x}$, which is a representative case. As above, we find that the total $\Delta\kappa_{xx}$ is the result of contributions spanning the whole phonon spectrum, and dominated by the changes in mean free paths. Also as above, we find that it is the change in the phonon lifetimes what controls $\Delta F_{j,\lambda}$; yet, at variance with the case of the E_z -fields, the present effect cannot be attributed to a general shift of frequencies. Indeed, we find that the E_x -field tends to harden the phonon spectrum (e.g., we obtain $\bar{\nu} = 10.02$ THz for $E_x = 0.5 \times E_{\text{coe},x}$). According to our above argument to explain the response to E_z -fields, the larger frequencies should result in longer lifetimes and an increased conductivity; yet, the effect of the perpendicular fields is just the opposite, with increased resistivity. Interestingly, a further analysis of our results reveals that, in this case, the field-dependence of the lifetimes is dominated by the three-phonon scattering matrix $V_{\lambda\lambda'\lambda''}$, which controls the phonon decay as $\tau_\lambda^{-1} \sim |V_{\lambda\lambda'\lambda''}|^{237}$. More specifically, we find that the E_x -field activates a large number of new scattering processes due to the symmetry breaking that it causes. (An E_z -field does not change the symmetry of PTO's P_z -polarized phase, and the proliferation of scattering events does not occur in that case.) This effect affects the whole phonon spectrum, and its magnitude naturally scales with the structural symmetry breaking caused by E_x , which is rather considerable given the large dielectric response of PTO to such a perturbation (for the corresponding susceptibility we obtain $\chi_{xx} \approx 304$; see Figure 1). Such a strong response to a transversal field is related to the “easy polarization rotation” that is well-known in FE perovskite oxides^{44,45}.

Interestingly, we also observe a field-induced coupling of the x and z directions – i.e., those along which the initial \mathbf{P} and the applied E_x -field are oriented – in the thermal conductivity tensor. We obtain values of κ_{xz} and κ_{zx} that are not negligible, of the same order of those in porous^{46,47} or amorphous materials⁴⁸. Their tempera-

ture dependence for applied fields is shown in the SM. This non-zero components imply that, e.g., a thermal gradient along x results in a heat flux, not only along x , but also along z .

In conclusion, we have reported evidence of the coupling between electric field and thermal conductivity in a ferroelectric perovskite. We have shown that an electric field perpendicular to the spontaneous polarization greatly increases the thermal resistivity, the underlying physical mechanism being the breaking of the symmetry of the lattice, which activates new scattering processes with a concomitant reduction of the lifetimes of phonons throughout the vibrational spectrum. On the other hand, for parallel fields that do not activate new scattering processes, we observe a linear variation of the thermal conductivity, which can grow or decrease depending on the sign of the applied field. This linear effect is controlled by the overall hardening/softening of the phonon modes. The predicted behaviors open the way to a fully-electric control of phonon transport. As the underlying physical principle is the manipulation of polar modes, these results can potentially be extended to a broader class of materials, possibly with even larger responses. Finally, we note that the symmetry breaking that leads to the largest changes in the thermal conductivity can also be

achieved in other ways, such as mechanical strains, that do not involve electric fields. Implementations of these concepts in a realistic device will have to take into account that substrates and additional layers will provide alternative heat transport channels and that the thermal contact resistance^{49,50} may complicate our taking advantage of the controllable transport properties of the ferroelectric layer. These issues, however, admittedly fall beyond the scope of the present manuscript.

ACKNOWLEDGMENTS

J.A.S.-B., H.A. and R.R. acknowledge financial support by the Ministerio de Economía, Industria y Competitividad (MINECO) under Grants No. FEDER-MAT2013-40581-P, No. FEDER-MAT2017-90024-P and the Severo Ochoa Centres of Excellence Program under Grant No. SEV-2015-0496 and by the Generalitat de Catalunya under Grants No. 2014 SGR 301 and No. 2017 SGR 1506. J.Í. acknowledges the support of the Luxembourg National Research Fund through the PEARL program (Grant No. FNR/P12/4853155 COFERMAT).

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- ¹ D. G. Cahill, W. K. Ford, K. E. Goodson, G. D. Mahan, A. Majumdar, H. J. Maris, R. Merlin, and S. R. Phillpot, *J. Appl. Phys.* **93**, 793 (2003).
 - ² L. D. Hicks and M. S. Dresselhaus, *Phys. Rev. B* **47**, 16631 (1993).
 - ³ D. Li, Y. Wu, P. Kim, L. Shi, P. Yang, and A. Majumdar, *Appl. Phys. Lett.* **83**, 2934 (2003).
 - ⁴ E. S. Toberer, L. L. Baranowski, and C. Dames, *Annu. Rev. Mater. Res.* **42**, 179 (2012).
 - ⁵ D. G. Cahill, P. V. Braun, G. Chen, D. R. Clarke, S. Fan, K. E. Goodson, P. Keblinski, W. P. King, G. D. Mahan, A. Majumdar, H. J. Maris, S. R. Phillpot, E. Pop, and L. Shi, *Appl. Phys. Rev.* **1**, 011305 (2014).
 - ⁶ M. N. Luckyanova, J. Garg, K. Esfarjani, A. Jandl, M. T. Bulsara, A. J. Schmidt, A. J. Minnich, S. Chen, M. S. Dresselhaus, Z. Ren, E. A. Fitzgerald, and G. Chen, *Science* **338**, 936 (2012).
 - ⁷ J. Ravichandran, A. K. Yadav, R. Cheaito, P. B. Rossen, A. Soukiassian, S. J. Suresha, J. C. Duda, B. M. Foley, C.-H. Lee, Y. Zhu, A. W. Lichtenberger, J. E. Moore, D. A. Muller, D. G. Schlom, P. E. Hopkins, A. Majumdar, R. Ramesh, and M. A. Zurbuchen, *Nat. Mater.* **13**, 168 (2013).
 - ⁸ M. Maldovan, *Nat. Mater.* **14**, 667 (2015).
 - ⁹ M. Terraneo, M. Peyrard, and G. Casati, *Phys. Rev. Lett.* **88**, 094302 (2002).
 - ¹⁰ C. W. Chang, D. Okawa, A. Majumdar, and A. Zettl, *Science* **314**, 1121 (2006).
 - ¹¹ W. Kobayashi, Y. Teraoka, and I. Terasaki, *Appl. Phys. Lett.* **95**, 171905 (2009).
 - ¹² R. Rurali, X. Cartoixà, and L. Colombo, *Phys. Rev. B* **90**, 041408 (2014).
 - ¹³ X. Cartoixà, L. Colombo, and R. Rurali, *Nano Lett.* **15**, 8255 (2015).
 - ¹⁴ N. Li, J. Ren, L. Wang, G. Zhang, P. Hänggi, and B. Li, *Rev. Mod. Phys.* **84**, 1045 (2012).
 - ¹⁵ G. Groetzinger, *Nature* **135**, 1001 (1935).
 - ¹⁶ C. E. Berry, *J. Chem. Phys.* **17**, 1355 (1949).
 - ¹⁷ R. P. Gairola and B. S. Semwal, *J. Phys. Soc. Jpn.* **43**, 954 (1977).
 - ¹⁸ G. Qin, Z. Qin, S.-Y. Yue, Q.-B. Yan, and M. Hu, *Nanoscale* **9**, 7227 (2017).
 - ¹⁹ H. H. Barrett and M. G. Holland, *Phys. Rev. B* **2**, 3441 (1970).
 - ²⁰ W. H. Huber, L. M. Hernandez, and A. M. Goldman, *Phys. Rev. B* **62**, 8588 (2000).
 - ²¹ M. E. Lines, *Phys. Rev.* **177**, 797 (1969).
 - ²² K. M. Rabe, C. H. Ahn, and J. Triscone, eds., *Physics of Ferroelectrics: A Modern Perspective* (Springer Berlin Heidelberg, Berlin, Heidelberg, 2007).
 - ²³ J. A. Seijas-Bellido, C. Escorihuela-Salayero, M. Royo, M. P. Ljungberg, J. C. Wojdeł, J. Íñiguez, and R. Rurali, *Phys. Rev. B* **96**, 140101 (2017).
 - ²⁴ M. Royo, C. Escorihuela-Salayero, J. Íñiguez, and R. Rurali, *Phys. Rev. Materials* **1**, 051402 (2017).
 - ²⁵ J. C. Wojdeł, P. Hermet, M. P. Ljungberg, P. Ghosez, and J. Íñiguez, *J. Phys. Condens. Matter* **25**, 305401 (2013).
 - ²⁶ P. García-Fernández, J. C. Wojdeł, J. Íñiguez, and J. Junquera, *Phys. Rev. B* **93**, 195137 (2016).
 - ²⁷ P. Zubko, G. Catalan, A. Buckley, P. R. L. Welche, and J. F. Scott, *Phys. Rev. Lett.* **99**, 99 (2007).
 - ²⁸ J. C. Wojdeł and J. Íñiguez, *Phys. Rev. Lett.* **112**, 247603 (2014).
 - ²⁹ J. C. Wojdeł and J. Íñiguez, *Phys. Rev. B* **90**, 014105 (2014).
 - ³⁰ P. Zubko, J. C. Wojdeł, M. Hadjimichael, S. Fernandez-

- Pena, A. Sené, I. Luk'yanchuk, J. Triscone, and J. Íñiguez, *Nature* **534**, 524 (2016).
- ³¹ P. Shafer, P. García-Fernández, P. Aguado-Puente, A. R. Damodaran, A. K. Yadav, C. T. Nelson, S.-L. Hsu, J. C. Wojdeł, J. Íñiguez, L. W. Martin, E. Arenholz, J. Junquera, and R. Ramesh, *Proc. Natl. Acad. Sci. (USA)* **115**, 915 (2018).
- ³² See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.97.184306> for the details on the computational methods.
- ³³ A. R. Damodaran, J. D. Clarkson, Z. Hong, H. Liu, A. K. Yadav, C. T. Nelson, S.-L. Hsu, M.-R. McCarter, K.-D. Park, V. Kravtsov, A. Farhan, Y. Dong, Z. Cai, H. Zhou, P. Aguado-Puente, P. García-Fernández, J. Íñiguez, J. Junquera, A. Scholl, M. B. Raschke, L.-Q. Chen, D. D. Fong, R. Ramesh, and L. W. Martin, *Nat. Mater.* **16**, 1003 (2015).
- ³⁴ P. Aguado-Puente and J. Junquera, *Phys. Rev. B* **85**, 184105 (2012).
- ³⁵ B. K. Sahoo, *J. Mater. Sci.* **47**, 2624 (2012).
- ³⁶ A. Togo and I. Tanaka, *Scr. Mater.* **108**, 1 (2015).
- ³⁷ W. Li, J. Carrete, N. A. Katcho, and N. Mingo, *Comp. Phys. Commun.* **185**, 1747 (2014).
- ³⁸ S. Tamura, *Phys. Rev. B* **27**, 858 (1983).
- ³⁹ W. Li, N. Mingo, L. Lindsay, D. A. Broido, D. A. Stewart, and N. A. Katcho, *Phys. Rev. B* **85**, 195436 (2012).
- ⁴⁰ P. Torres, A. Torelló, J. Bafaluy, J. Camacho, X. Cartoixà, and F. X. Alvarez, *Phys. Rev. B* **95**, 165407 (2017).
- ⁴¹ B. Xu, J. Íñiguez, and L. Bellaiche, *Nat. Commun.* **8**, 15682 (2017).
- ⁴² In the specific case of longitudinal fields this is not only an *average* behavior: all the frequencies increase (decrease) in presence of a parallel (antiparallel) external electric field.
- ⁴³ A. Mercy, J. Bieder, J. Íñiguez, and P. Ghosez, *Nat. Commun.* **8**, 1677 (2017).
- ⁴⁴ H. Fu and R. E. Cohen, *Nature* **403**, 281 (2000).
- ⁴⁵ L. Bellaiche, A. García, and D. Vanderbilt, *Phys. Rev. Lett.* **84**, 5427 (2000).
- ⁴⁶ G. Gesele, J. Linsmeier, V. Drach, J. Fricke, and R. Arens-Fischer, *J. Phys. D: Appl. Phys.* **30**, 2911 (1997).
- ⁴⁷ R. Dettori, C. Melis, X. Cartoixà, R. Rurali, and L. Colombo, *Phys. Rev. B* **91**, 054305 (2015).
- ⁴⁸ B. L. Zink, R. Pietri, and F. Hellman, *Phys. Rev. Lett.* **96**, 055902 (2006).
- ⁴⁹ S. Yazji, E. A. Hoffman, D. Ercolani, F. Rossella, A. Piantanti, A. Cavalli, S. Roddaro, G. Abstreiter, L. Sorba, and I. Zardo, *Nano Res.* **8**, 4048 (2015).
- ⁵⁰ 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).