Ab Initio Phonon Dispersions for PbTe

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We report first principles calculations of the phonon dispersions of PbTe both for its observed structure and under compression. At the experimental lattice parameter we find a near instability of the optic branch at the zone center, in accord with experimental observations. This hardens quickly towards the zone boundary. There is also a very strong volume dependence of this mode, which is rapidly driven away from an instability by compression. These results are discussed in relation to the thermal conductivity of the material.

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I. INTRODUCTION

The thermoelectric performance of a material is quantified using a dimensionless, temperature dependent figure of merit, $ZT = \sigma S^2 T / \kappa$, where $\sigma$ is the electrical conductivity, $\kappa$ is the thermal conductivity, and $S$ is the thermopower. Thus it is clear that high thermoelectric performance is generally found in materials with low thermal conductivity, and in fact various strategies for lowering thermal conductivity based on phonon scattering have been employed. These include alloying to produce mass disorder as in SiGe, the use of materials with large complex unit cells, and the use of materials with rattling ions, such as filled clathrate materials. In this regard rocksalt structure PbTe is a remarkable thermoelectric material. It is based on a small, high symmetry unit cell, has high coordination of both atomic species (6-fold), and contains no obvious rattling ion. Nonetheless, n-type PbTe has high values of $ZT$ above room temperature and as such was used in spacecraft power generators. It also has low thermal conductivity, reported as 2.3 W/(m K) at ambient temperature. Recently, a family of so-called LAST compounds based on intergrowths of PbTe and Ag$_x$SbTe$_2$ have been shown to have values of $ZT$ well above unity, and additionally quantum dot systems based on PbTe have also shown high values of $ZT$.

Thermal properties of materials in general rest on the phonon dispersions. While electronic and related properties of PbTe has been rather extensively studied using first principles methods, the phonon dispersions have not been reported. The purpose of this paper is to report these dispersions, as obtained within density functional theory.

The calculations reported here were done within the framework of density functional theory primarily using the local density approximation. The quantum espresso code was used with norm conserving pseudopotentials to obtain the phonon dispersions via linear response. Convergence tests were performed to determine the needed planewave basis cut-off and zone sampling. The results shown used a planewave basis set with a 60 Ry cutoff and an 6x6x6 special $k$-points Brillouin zone sampling. W e performed convergence tests with a 75 Ry cutoff and an 8x8x8 special $k$-points Brillouin zone sampling but found no significant differences in phonon frequencies. In addition, some calculations were done with the linearized augmented planewave (LAPW) method including local orbitals. These provide a check for the pseudopotential results. Calculations were performed as a function of lattice parameter. The calculated LAPW LDA lattice parameter is 6.39Å, which is slightly more than 1% smaller than the experimental room temperature lattice parameter of 6.464Å, and within 1% of the 120K value of 6.438Å. For comparison the calculated LAPW lattice parameter within the generalized gradient approximation of Perdew, Burke and Ernzerhof is 6.57Å, which is further from experiment than the LDA. We therefore use the LDA, and perform calculations as a function of lattice parameter. Assuming that PbTe behaves like other materials with soft phonons, comparison with experiment should be done for the phonon dispersions calculated at the experimental lattice parameter.
III. RESULTS AND DISCUSSION

Our main results are the phonon dispersions, which are given in Fig. 1. As may be seen, PbTe is near a zone center phonon instability, associated with the transverse optic (TO) mode. This is an inversion center breaking phonon, and would lead to a ferroelectric ground state if it were actually unstable. This is not a surprising result and in particular is in accord with experimental studies of NaCl structure group IV tellurides. The related materials SnTe and GeTe are in fact ferroelectric, with rhombohedral ground states corresponding to freezing in of the soft TO mode with displacements along a [111] direction. [22, 23, 24]

The ferroelectricity of GeTe has been studied in detail using first principles calculations by Rabe and co-workers, [22, 23, 24] who showed quantitative agreement between the predictions of LDA calculations and experiment. Bussmann-Holder used model calculations to investigate the phase diagrams of various alloys including PbTe-SnTe and PbTe-GeTe and made arguments for the nearness of PbTe to ferroelectricity. [22] In fact it was known that PbTe shows a dielectric constant that increases at low T as well as a TO phonon mode that decreases in frequency as the temperature is lowered, [23, 24] although the detailed T dependence is complicated by a doping level dependence. In any case, Burhard and co-workers [24] obtained obtained a very soft frequency of 17.5 cm\(^{-1}\) from optical measurements on PbTe films. This value is consistent with the very low value of 12 cm\(^{-1}\) that we obtain at the reported experimental lattice parameter. This difference of \(\sim\) 5 cm\(^{-1}\) is well within the usual errors of LDA calculations.

Comparing the two panels of Fig. 1 one may note a strong volume dependence of the TO phonon frequency around the zone center. This frequency at Γ is plotted as a function of lattice parameter in Fig. 2. As may be seen there is a very strong volume dependence to the soft TO mode. Compressing the lattice parameter to 6.40 Å, which is less than 0.6% smaller than the 120K value, more than doubles the TO frequency from 12 cm\(^{-1}\) to 27 cm\(^{-1}\). The LO mode on the other hand shows a quite ordinary, modest volume dependence. While such strong volume dependences of soft mode phonon frequencies are unusual they have been noted before in complex oxide ferroelectrics, such as Pb(Zr,Ti)O\(_3\), BaTiO\(_3\) and KNbO\(_3\). [21, 30, 31] The present results show that there is a similar behavior in PbTe in spite of the much simpler structure of this material in comparison with the oxide ferroelectrics.

Returning to the issue of the thermoelectric properties of PbTe, the material clearly does not involve alloying with different mass ions or a large complex unit cell to lower thermal conductivity. Furthermore, the acoustic modes are not anomalously soft. One mechanism that has been discussed in the context of thermoelectric materials is the use of so-called rattlers. These are loosely bound atoms in a crystal structure that couple to the low frequency part of the phonon spectrum leading to scattering. One may ask then if there is an analogy between the soft TO vibrations near the zone center and a material containing rattlers. One such connection can be made based on the strong volume dependence. Longitudinal acoustic (LA) vibrations are compressive waves...
FIG. 3: Calculated energy as a function of phonon amplitude for the Γ point TO mode, with displacements along the tetragonal and rhombohedral directions for the experimental 300K lattice parameter of 6.464 Å. The horizontal line corresponds to $kT$ for $T=300K$.

and so the strong volume dependence of the TO mode implies strong anharmonic coupling between the TO branch and the LA phonons. Furthermore, we find that the TO modes are highly anharmonic themselves. Fig. 3 shows the calculated energy as a function of TO mode amplitude at the experimental volume. As may be seen the energy surface remains very soft up to large amplitude $\sim 0.1$ Å, and then starts to stiffen in a quite anharmonic way. This may be seen, e.g., from the difference between [001] and [111] energies, which arises due to the anharmonicity. For large amplitudes the softest direction is [111] in agreement with the experimental ground state of GeTe. However, even for [001] displacements the energy surface is very soft implying large amplitude vibrations even at room temperature. However, it should be noted that the TO mode is only soft near the zone center, and so the mean square displacement will be less than that implied by the position of the $kT=300K$ line on Fig. 3. This also means that unlike rattling modes in clathrates, for example, the soft TO modes in PbTe are strongly $k$-dependent, similar to the acoustic modes.

IV. CONCLUSION

While the above results do not provide a quantitative description of the thermal conductivity of PbTe they do show that there are unusual features of the phonon spectrum that are generally associated with reduced thermal conductivity. In particular we find very soft TO phonon branches near the zone center as may be expected in a material near ferroelectricity. Importantly, these modes are very volume dependent which implies strong anharmonic coupling to longitudinal acoustic modes. Furthermore, although the TO modes are quite $k$-dependent, which is not an indicator of low thermal conductivity, they are also highly anharmonic, as seen from the Fig. 3. This normally will lead to increased scattering at high temperature and accordingly reduced thermal conductivity.

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