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High-temperature thermoelectric performance of heavily doped PbSe

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We present a model calculation, employing first-principles calculations as well as empirical data, which suggests that properly hole-doped bulk PbSe may show a Seebeck coefficient as high as 230 μV/K, in a temperature regime in which the lattice thermal conductivity is rather small. It may therefore show a figure-of-merit ZT as high as 2 for temperatures of 1000 K. Heavily doped p-type PbSe may offer better thermoelectric performance than the sister material, optimized PbTe, for high-temperature applications such as power generation.

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I. INTRODUCTION

The lead chalcogenides, such as PbTe and PbSe, have been under consideration for several decades as semiconductors of potential interest in such diverse fields as electronics and thermoelectrics. PbTe, in particular,[1–5] has been found to have a thermoelectric figure-of-merit ZT (Ref. 6) of approximately unity at a temperature of 500 K, which might find application in the recovery of waste heat from motor vehicles and other sources. Recent efforts at Thallium doping PbTe have also shown success, with a ZT figure of 1.5 at 773 K reported by Heremans *et al.*,[7] and surprising additional promise has been shown by the "LAST" materials,[8] $AgPb_mSbTe_{2+m}$ ($m=10$ or 18) which also have ZT above that of standard PbTe.

Perhaps because of the relative success of PbTe in the range around 500 K, the sister material PbSe has received comparatively little attention, as it usually shows a lower figure-of-merit in this temperature range. Interestingly, however, doped PbSe shows[9] a thermoelectric voltage (usually referred to as the Seebeck coefficient) which does not exhibit the usual saturation and "turn-over" at high temperature, but continues increasing even at 1000 K, thus making it a potential material, superior to PbTe, for high-temperature applications such as power generation. Finally from a practical perspective PbSe has two important advantages relative to PbTe: first, Se is more commonly available and less expensive than Te, and second, the melting point of PbSe is substantially higher, at 1340 K, than PbTe at 1190 K. This higher decomposition temperature takes on particular importance in applications such as vehicle waste heat recovery, where durability under severe and highly variable conditions is of great importance.

Detailed experimental consideration of the thermoelectricity in doped PbSe has thus far been lacking, with few recent studies[9,10] in this area. The most significant work was performed by Alekseeva *et al.*,[9] and the doping levels in this study were not well quantified. In addition, the electrical conductivity in this study did not follow the canonical (1/T) form for electron-phonon scattering (the primary relaxation mechanism in heavily doped semiconductors) at high temperatures, but decreased significantly more rapidly at high temperature, which, assuming the Wiedemann- Franz relation,[11] would lead to a low electronic thermal conductivity. Since the figure of merit is partially determined by the ratio of lattice and electronic thermal conductivity, (in addition to the thermopower) this leads to the possibility that more carefully prepared samples could show a substantially enhanced ZT, if the electrical conductivity and electronic thermal conductivity show a more typical behavior.

In this paper, we address this possibility quantitatively by constructing a model, based on first-principles calculations of the Seebeck coefficient as well as empirical data[12] for the temperature and doping dependence of the mobility of doped PbSe. We find that ZT as high as 2 at 1000 K may be possible in hole-doped samples with a carrier concentration p of 0.007–0.01 holes/formula unit, or about $1.2-1.7\times10^{20}/\mathrm{cm}^3$.

II. MODEL

We calculated the band structure of PbSe with the WIEN2K package,[13] using the generalized gradient approximation (GGA) as well as spin-orbit coupling, yielding a band gap of approximately 65 meV, in good agreement with other published results.[14,15] From the converged calculations, we employed the BOLTZTRAP software[16] to calculate the thermopower S, within the constant relaxation time approximation, which in general is a good approximation as long as the scattering rate $\tau(E)$ does not vary radically on an energy scale of a few kT, T the temperature. Its prime advantage is that detailed assumptions about the nature of the scattering are not necessary. It has been used with quantitative accuracy in calculating thermopowers of metals and doped semiconductors.[17–20] The approximation is in this case aided by the experimental hole and electron mobilities being essentially equal. The canonical expressions for $S(T)$ and the related quantity the conductivity $\sigma(T)$ are as follows [note that $-\mathrm{sech}^2(x)=4df/dx$, f the Fermi function]:

$$S(T) = -\frac{1}{3eT\sigma(T)}\int_{-\infty}^{\infty} de\sigma(E)(E-\mu)\mathrm{sech}^2[(E-\mu)/2T] \tag{1}$$

$$\sigma(T) = \int_{-\infty}^{\infty} dE\sigma(E)\mathrm{sech}^2[(E-\mu)/2T] \tag{2}$$

TABLE I. Mobility temperature power relations extracted from data of Schlichting.

Power relation exponents n (cm^{-3})	x
0.0039×10^{20}	−2.56
0.032	−1.61
0.25	−1.40
1.1	−1.13

$$\sigma(E) = N(E)v^2(E)\tau(E), \tag{3}$$

where $\tau(E)$ is the scattering time, $v(E)$ the Fermi velocity and $N(E)$ the density of states. We have suppressed the tensor indices, which are not relevant for cubic PbSe, and note that the conductivity $\sigma(E)$ in reality involves a Brillouin-zone sum of the quantity $\sigma_k = N(k)v_k^2\tau_k$ for energy eigenvalues $\varepsilon_k = E$.

The second element of the model is the temperature and doping dependence of the thermal conductivity. Assuming the Wiedemann-Franz relation, the figure of merit ZT can be rewritten as

$$\mathrm{ZT} = S^2 r/L_0, \tag{4}$$

where L_0 is the Lorenz number$=2.45\times 10^{-8}$ W/m^2 K and r is the ratio of electronic and total thermal conductivity. The Wiedemann-Franz relation is generally a good assumption for degenerate, heavily doped semiconductors and metals. Reference 21 has a detailed discussion of the accuracy of this assumption; briefly, as long as the chemical potential is not in the gap or near the band edge, the relationship holds. For the heavy dopings studied here, $\mu - E_{gap}$ generally exceeds 0.2 eV. We assume the Wiedemann-Franz law here. In this case, the electronic thermal conductivity is simply $L_0\sigma T$, so that with $\sigma = ne\mu_m$, with n the carrier concentration and μ_m the mobility, calculating the electronic thermal conductivity then reduces to calculating, or estimating, the mobility as a function of temperature and doping. Any first-principles calculation of the conductivity or mobility requires knowledge of the scattering time, which we do not have. The best course of action then to estimate $\sigma(T)$ is to perform a careful extrapolation of the available experimental data. We note that the Seebeck coefficient involves a *ratio* of a thermally weighted $\sigma(E)$ and $\sigma(T)$ (both $\propto \tau$) and can therefore be calculated reliably from first-principles absent knowledge of the scattering time, unlike $\sigma(T)$.[22]

There is presently little PbSe mobility data at the heavily doped ($p = 1-3\times 10^{20}$/cm^3) concentrations where S is substantial, so that it is necessary to extrapolate from lower concentration data, for which the primary reference is the work of Schlichting *et al.*[12] Much of this data is at concentrations of $10^{17}-10^{18}$ cm^{-3} and $T \leq 300$ K, where the mobility follows an approximate power relation $\mu_m \sim T^{-2.2}-T^{-2.5}$. However, as indicated in Table I, for larger concentrations the exponent changes and approaches −1. This mobility exponent is characteristic of electron-phonon scattering, as is expected to dominate in the heavily doped high-temperature limit, where the expected behavior is that of a metal with electron- phonon scattering. To assess this quantitatively we briefly reprise the work of Pickett,[23] who showed that T-linear resistivity (or equivalently, $1/T$ mobility behavior) obtains over a wide temperature range for a great variety of phonon density-of-states (PDOS) $F(\Omega)$. The scattering rate $\hbar\Gamma(T)$ given a transport coupling constant α_{tr} and PDOS $F(\Omega)$ is given as

$$\hbar\Gamma(T) = 4\pi k_B T \int \frac{d\Omega}{\Omega}\alpha_{tr}^2 F(\Omega)\left(\frac{\Omega/2k_BT}{\sinh(\Omega/2k_BT)}\right)^2. \tag{5}$$

Assuming $F(\Omega) \propto \Omega^2$ for $\Omega < \Omega_{Debye}$, the simplest possible model, one may calculate the scattering rate and finds, as depicted in Fig. 1, that this is essentially linear for $T > \Omega_D = 183$ K for PbSe. This can also be seen directly from the above equation, in which for high temperatures the temperature-dependent term $\frac{\Omega/2k_BT}{\sinh(\Omega/2k_BT)}$ becomes simply unity. Since our interest here is $T \gtrsim 500$ K ~ 3 Ω_D for PbSe, we conclude that $\mu_m \sim 1/T$ is an excellent approximation for the present work. A detailed first-principles calculation of scattering times[21] in $\mathrm{Bi_2Te_3}$ essentially leads to the same conclusion.

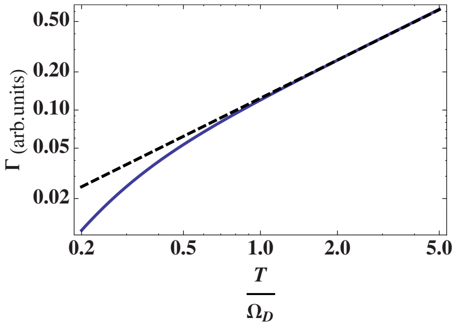

FIG. 1. (Color online) The scattering rate Γ (arbitrary units) for electron-phonon scattering as a function of temperature, note the logarithmic scale for both axes. A T-linear line (dashed) is shown for comparison. Note that $\mu_m \propto 1/\Gamma(T)$.

We now move to the doping dependence of the mobility. At the concentrations of interest, the mobility decreases substantially with increased concentration, and a simple linear regression of Schlichting's data yields $\mu_M \propto n^{-0.6}$. We have chosen the proportionality constants to match the experimental mobility values at $T = 300$ K and $N = 1.1\times 10^{20}$/cm^3 (note that in Schlichting's data this data point was in fact electron-doped, but in this material the hole and electron mobilities are very similar, at least at moderate carrier concentrations).

The final piece of the model is the lattice thermal conductivity κ_l which was measured for undoped PbSe by Sharkawy *et al.*[24] We assume that this term is independent of carrier concentration since even the heavy dopings studied here amount to at most 0.02 holes/f.u., which is unlikely to affect lattice dynamics significantly. For the temperature dependence, we use the relationship $\kappa_l = C_l v_l \ell_l$, noting that for the temperature range of interest, far above $\Omega_D = 183$ K, C_l is constant while the mean free path $\ell \propto 1/T$, a relationship reasonably consistent with Sharkawy's data. This data set

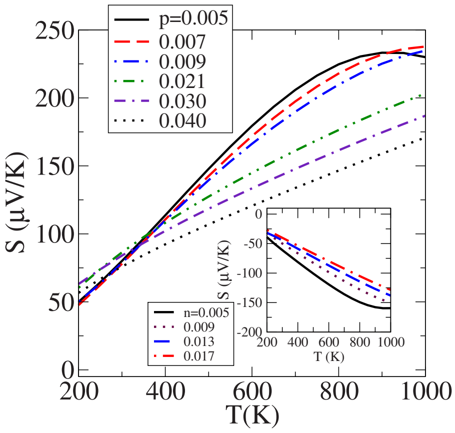

FIG. 2. (Color online) The thermopower S, in μV/K, at various hole (main figure) and electron (inset) doping levels. The hole dopings increase from top to bottom, while the electron dopings decrease from top to bottom.

gives κ_l as 1.7 W/m K at 300 K,[25] which fixes the proportionality constant.

III. RESULTS

We begin with the thermopower S. As depicted in Fig. 2, for dopings in the range of 0.005–0.01 holes/f.u., this approaches 230 μV/K at 1000 K. We note considerable asymmetry between the electron and hole-doped results, with electron-doping resulting in a maximum absolute thermopower of only 160 μV/K (inset) This thermopower difference is related to the existence of a flat, high-mass, high DOS band roughly 0.35–0.4 eV below the gap, as depicted in Fig. 3, which enhances the thermopower at heavy hole dopings. A similar effect is present in hole-doped PbTe,[26] where the flat-band lies between 0.2 and 0.25 eV below the gap. In PbSe, except for this band, the valence and conduction bands are roughly symmetric about the middle of the gap at the L-point in Fig. 3(a). For neither hole nor electron dopings in the range studied is the usual "rollover" effect caused by double-sign conduction significant, which is a result of the low density-of-states on both sides of the band gap, which means that the heavy dopings studied here occasion substantial motion of the chemical potential and hence the attenuating effect of the thermal factor in Eq. (1) reduces the impact of the opposite band. At lower dopings of 0.001–0.003 holes or electrons per formula unit (not shown) the rollover indeed appears.

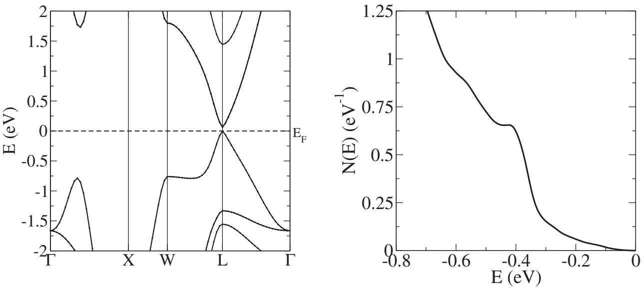

FIG. 3. The band structure and density-of-states of PbSe. Note the flat band 0.6 eV below the gap in the band structure plot, and the rapid change in the density-of-states between −0.35 and −0.4 eV below the gap, indicating another flat band (not shown on the band structure as it is not on a symmetry axis. Constant-energy contours for this band lie fairly near a line connecting the L-points of the Brillouin zone.)

The "flat-band" is in fact located at a substantially higher hole concentration than might first be expected; the first-principles calculations yield p=approximately 0.07/f.u. for the chemical potential located at this band, compared to the 0.007–0.009 holes/f.u. at which ZT is maximized. The basic reason ZT is maximized at this lower concentration, and not $p=0.07$, is that as one dopes deeper into the valence band, the portion of available states located *above* the chemical potential, and hence of the "wrong" sign for maximizing S, increases; this is the reason why thermopower usually decreases monotonically with increasing carrier concentration. The actual point of maximum S, and ZT, is the result of a "balancing act" between the effects of this double-sign conduction and the generally S-enhancing heavy-mass band, and is also temperature dependent. As a final point, we note that for the calculation of ZT, this also depends on the mobility, which will generally decrease as the heavy-mass band is approached, as included in our calculation.

As stated previously, the underestimation of the band gap means that the thermopower S is itself understated, since increasing the band gap to the experimental value would reduce the bipolar conduction, which itself acts to *reduce* S. Without performing additional calculations, it is difficult to estimate the increase in thermopower that would result if the experimental gap were used, but we note that the S and ZT values described here would, at a minimum, still obtain at the doping values indicated. It is possible that the dopings for maximum overall ZT values could be slightly reduced from the values cited here. Since the shape of the bands—critically affecting the thermopower—and the band gap are not independent entities in a real material, we have not artificially adjusted the band gap to match experiment.

These thermopower results are generally consistent with the results of Alekseeva, who found thermopowers as high as 280 μV/K on doped PbSe samples.

The substantial thermopowers in the hole-doped materials lead to comparatively high figures-of-merit; as indicated in Fig. 4, for dopings of 0.007–0.009 holes/f.u. ZT's of roughly 2 are achievable at 1000 K. This is substantially higher than that found by Alekseeva and underscores the need for precise control of doping. With our extrapolated mobility we estimate that under these conditions no more than 10–15 % of the total thermal conductivity originates from the lattice; if this estimate understates reality by a factor of two one still attains a maximum ZT of 1.7–1.8. As expected, the figure-of-merit (shown in the inset of Fig. 4) is substantially lower for the electron-doped materials, due almost entirely to the differing behavior of S.

In Fig. 5 we show the "power factor" $=S^2\sigma$ for the hole-doped materials, which is maximal at somewhat higher dopings than ZT is, due largely to the increased conductivity at larger dopings (note that while μ_m decreases with doping as $n^{-0.6}$, since $\sigma = ne\mu_m$, σ increases with doping).

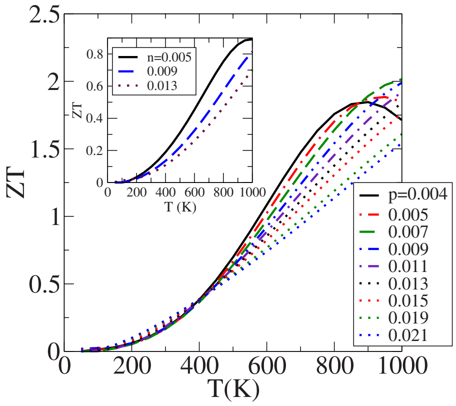

FIG. 4. (Color online) The calculated figure-of-merit ZT for doped PbSe at various hole concentrations (main plot) and electron concentrations (inset). At 800 K, the figure-of-merit is a monotonically decreasing function of doping, both for holes and electrons; at 1000 K ZT is maximized for $p=0.007-0.009$ holes/f.u.

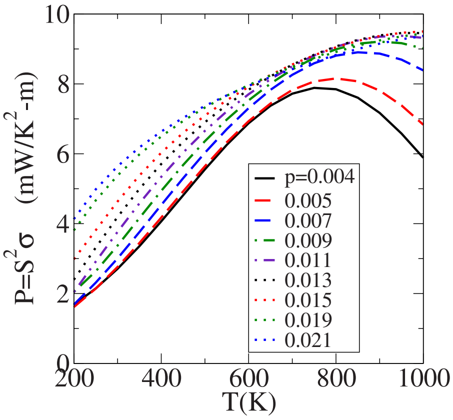

FIG. 5. (Color online) The calculated power factor for doped PbSe at various hole concentrations. At high temperature, the power factor increases up to approximately 0.015 holes/f.u., after which it decreases.

IV. DISCUSSION

The results of the previous section suggest that hole-doped PbSe may show renewed promise as a potential high-temperature thermoelectric, if doping can be closely controlled and the temperature and doping dependence of the mobility follow expected trends. We note that if the noncanonical mobility behavior (i.e., decaying much faster than $1/T$ at high temperature) observed by Alekseeva *et al.* is found to exist even for carefully doped samples, it is less likely that ZT's of 2 will be achievable. One reason this may happen is that the heavy doping studied here, outside the range of existing data, may cause hole mobility to be less than assumed, due to the influence of the heavy flat bands below the gap. For low doping, hole and electron mobilities are experimentally equal, as we assumed, but this assumption may break down at larger hole doping. This represents the single largest source of uncertainty into the calculated ZT's, and could lower ZT significantly. We note also that, conversely, the understatement of the band gap, as discussed previously, will tend to underestimate ZT. In any case, due to the present paucity of data on heavily hole-doped PbSe, we believe this material deserves further exploration as a possible high-temperature thermoelectric.

ACKNOWLEDGMENTS

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