Very heavily electron-doped CrSi$_2$ as a high-performance high-temperature thermoelectric material

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Abstract. We analyze the thermoelectric behavior, using first principles and Boltzmann transport calculations, of very heavily electron-doped CrSi$_2$ and find that at temperatures of 900–1250 K and electron dopings of 1–4 × 10$^{21}$ cm$^{-3}$, thermopowers as large in magnitude as 200 $\mu$V K$^{-1}$ may be found. Such high thermopowers at such high carrier concentrations are extremely rare, and suggest that excellent thermoelectric performance may be found in these ranges of temperature and doping.

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1. Introduction

Thermoelectric performance is typically quantified in terms of a dimensionless parameter ‘$ZT$’, defined as follows:

$$ZT = S^2 \sigma T / \kappa.$$  

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Here $S$ is the Seebeck coefficient, $\sigma$ the electrical conductivity, and $\kappa$ the thermal conductivity. High-performance thermoelectric materials are usually considered to have $ZT \sim 1$ or greater. The explicit form equation (1) suggests that a key requirement for a good thermoelectric is a high Seebeck coefficient (also known as the thermopower) at the temperature range of interest (generally of magnitude $200 \mu V \, K^{-1}$ or greater), along with low lattice thermal conductivity and good carrier mobility. Nearly all the good thermoelectrics known today—Bi$_2$Te$_3$, the filled skutterudites [1], TAGS-85 (tellurium, antimony, germanium, silver) [2], PbTe/PbSe [3]—satisfy these requirements, often through the use of heavy-mass bands as these enhance the thermopower for given carrier concentration.

The carrier concentration at which $ZT$ is optimum varies by material but is typically $10^{19} - 10^{21} \, \text{cm}^{-3}$, leading to the requirement for good thermoelectrics to be heavily doped semiconductors. Thus it was surprising when the layered hexagonal cobalt oxide NaCo$_2$O$_4$ was found to be a good thermoelectric with maximum $ZT$ exceeding unity at $T = 1000 \, K$ [4], but with a nearly metallic resistivity whose planar value approaches $10 \mu \Omega \, \text{cm}$ [5, 6] at low temperatures, and a carrier concentration $p$ at low temperature of roughly $3 \times 10^{21} \, \text{cm}^{-3}$. This material achieves its remarkable thermoelectric properties by the presence of extremely heavy band masses, compensating for its comparatively low mobility. The key feature of NaCo$_2$O$_4$ is its heavy $d$-bands, which are readily chemically doped.

Band structure calculations have proven to be a useful tool in the prediction of thermoelectric performance. For example, band structure calculations [7] predicted that, contrary to then-prevalent opinion, hole-doped PbSe would be a thermoelectric material superior to PbTe at high temperature—a prediction already confirmed by experiment [8]. Similarly, band structure calculations [9] predicted that excellent thermoelectric performance would occur in PbTe without need of the toxic element thallium—a prediction also already confirmed by experiments of Snyder and Kanatzidis [10, 11]. Finally, recent band structure calculations [12] predict that ZnO is not likely to be a good thermoelectric material at any temperature.

Here we discuss another heavy band mass material which may give good performance at high temperatures (in this case near 1250 K) despite relatively poor mobility and moderately high lattice thermal conductivity. The material CrSi$_2$ has been known as a thermoelectric for many years, but is commonly thought [13] not to be a good thermoelectric at elevated temperature due to its comparatively small band gap of 0.3–0.35 eV. Such a small band gap generally causes bipolar conduction, wherein the thermopower $S(T)$ decreases with increasing temperature (a negative for thermoelectric performance), and it is generally believed that this band gap precludes applications of CrSi$_2$ at temperatures more than about 600 K. The maximum observed $ZT$ [14, 15] is only 0.2 at 450 K, although these results suggest that performance better than this may be attainable above this temperature. In any case, the ‘rule’ [16] that band gaps should be at least six times maximum operating temperature would suggest that 600 K should be the maximum operating temperature of this material. However, this rests upon the assumption of a simple band structure and so exceptions are possible.

We find, based upon our first principles density functional and Boltzmann transport calculations, that thermopowers as high in magnitude as $200 \mu V \, K^{-1}$ may be found in this material, in a temperature range between 900 and 1250 K, and most surprisingly, at electron concentrations $n$ of $1-4 \times 10^{21} \, \text{cm}^{-3}$. We find that this material will perform well at high temperature despite having a rather high lattice thermal conductivity of $8 \, \text{W} \, (\text{mK})^{-1}$ [17] at
Figure 1. The calculated band structure for CrSi$_2$ in the hexagonal Brillouin zone. The valence band maximum is set to the energy zero. Note that the calculated band gap of 0.33 eV is in excellent agreement with the experimental value of 0.3–0.35 eV.

CrSi$_2$ attains this behavior through its remarkably heavy bands. Presented in figure 1 is the calculated band structure of this material—both valence and conduction bands show large regions of momentum space less than 0.5 eV from the band edge, in a hexagonal unit cell of $ab$-plane lattice constant 4.428 Å (note that the $c$-axis lattice constant is 6.368 Å) leading to the large band masses. In addition, the conduction bands show a remarkably flat band between L and H, and the right hand portion of M–H, with dispersion less than 0.1 eV, as well as a comparatively flat band between K and L. This heavy band is key for the n-type thermopower behavior, as we describe in the following section. Note also that while density functional methods often understate the band gap, here we match the experimental value of 0.3–0.35 eV very well; a possible reason for this is given in [18–20].

Our work in fact reproduces the previously calculated bandstructure of CrSi$_2$ well, as presented in these last references. Note that this band structure was confirmed by experiment in [21]. The principal message of this work is that this bandstructure is likely to lead to favorable thermoelectric properties at very heavy electron concentration.

2. Model and calculated results

Our results are calculated using first principles density functional theory in the Perdew–Burke–Ernzerhof [22] generalized gradient approximation, along with Boltzmann

Note that if a $1/T$ relationship is assumed for the lattice thermal conductivity, its value at 1250 K would be less than 2 W (m K)$^{-1}$, a value amenable to good thermoelectric performance.
Figure 2. The calculated planar (left) and c-axis (right) thermopower for CrSi₂. Note the excursions with magnitude greater than 200 $\mu$V K$^{-1}$; for this compound a doping of 0.1 electrons per unit cell is equivalent to $9.25 \times 10^{20}$ cm$^{-3}$.

transport theory. We used the linearly augmented plane-wave code WIEN2K [23] to calculate the bandstructure and the BoltzTrap code [24] to calculate the thermopower within the constant relaxation time approximation, which has been used with notable success [7, 24–30] to describe the thermopower of a large number of thermoelectric materials. The approximation is based upon the observation that scattering times generally do not vary greatly on a scale of $k_B T$ around the Fermi energy, the region important for transport.

All band structure calculations were performed to self-consistency with approximately 2000 $k$ points in the full Brillouin zone, while the transport calculations employed approximately 20 000 $k$ points. No internal coordinate optimization was performed as calculated forces within the experimental structure are already low. Muffin tin radii of 2.17$a_0$ (where $a_0$ is the Bohr radius) for Si and 2.47$a_0$ for Cr were used, along with an $R K_{\text{max}}$ of 7, where $R$ is the smallest muffin tin radius and $K$ the wavevector of the largest plane wave.

In figure 2 we present the calculated thermopower at several electron concentrations for temperatures up to 1500 K (note that the melting point of this compound is approximately 1711 K [31]). We note that the planar thermopower exceeds 200 $\mu$V K$^{-1}$ at 1250 K for dopings of 0.2 electrons per unit cell, and is just slightly less than this value at 1250 K for dopings of 0.3 electrons per unit cell, corresponding to a doping of $2.78 \times 10^{21}$ cm$^{-3}$. The c-axis thermopowers at these dopings are slightly lower than this, but in a polycrystalline sample, as would probably be used for applications, the thermopower in the direction of maximum electrical conductivity will tend to dominate the measured Seebeck coefficient. To assess this effect, we employ the canonical expressions for the transport function $\sigma(E)$ and the closely related quantity the electrical conductivity $\sigma(T)$:

$$\sigma(E) = N(E) v^2(E) \tau(E),$$

$$\sigma(T) = -\int_{-\infty}^{\infty} dE \sigma(E) f(E - \mu)/dE,$$

where $f$ is the Fermi function, $\tau(E)$ is the scattering time, $v(E)$ the Fermi velocity, $\mu$ the chemical potential and $N(E)$ the density of states. We have suppressed the tensor indices, and
Figure 3. The calculated $\sigma/\tau$ results in the indicated directions at 1250 K for a range of electron doping. Note that for dopings between 0.2 and 0.4 electrons per unit cell, the planar ($\sigma_{xx}$) values are roughly twice the $c$-axis values.

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note that the integrations in reality involve a Brillouin-zone sum of the quantity $\sigma_k = N(k) v_k^2 \tau_k$ for energy eigenvalues $\varepsilon_k = E$.

As shown in figure 3, the planar electrical conductivity $\sigma(T)/\tau$ is roughly two times larger than the $c$-axis values at the dopings of interest, so that the higher planar thermopower results will be found in practice.

In figure 4(a) we plot the Fermi surface for an electron doping level such that the zero-temperature Fermi level lies 0.19 eV within the conduction band, or a zero-temperature doping of approximately 0.3 electrons per unit cell. A strong two-dimensional sheet is found near the hexagonal Brillouin zone boundary, which will tend to enhance the thermopower for transport in this direction (i.e. $\Gamma - M$). We have checked that the semiconducting gap structure does not change at this heavy doping by performing additional calculations within the virtual crystal approximation at this doping (an additional 0.1 electrons per Cr); as seen in figure 4(b), while the position of the chemical potential, relative to the band edge of course changes, the value of the semiconducting gap and shape of the density-of-states are virtually unchanged.

Returning to the thermopower, we note in figure 2 substantial anisotropy between the planar and $c$-axis thermopower, with the $c$-axis thermopower generally showing much stronger effects of bipolar conduction—visible in the plots as a decrease of thermopower with temperature.

The reason for these differences in bipolar behavior may be found in the band structure plots of figure 1 (previous page) and the Fermi surface plot in figure 4. As indicated in figure 1, the conduction band structure contains three minima at M, K and L, with a flat band running from L to H, while the valence band contains one main maximum centered at the L point and relatively isotropic, as seen in examination of figures 1 and 4. The directions $\Gamma-K$, $M-K$, $A-L$
Figure 4. Left: the hexagonal CrSi$_2$ Brillouin zone, and calculated Fermi surface for the zero-temperature Fermi energy set 0.19 eV into the conduction band. Note the large two-dimensional band parallel to the zone face. Right: the density of states for stoichiometric CrSi$_2$ as well as that calculated within the virtual crystal approximation for an electron doping of 0.3 per unit cell. Note that the main effect of the doping is to change the Fermi energy relative to the band edge; the gap and density-of-states are largely unchanged. For this plot for the stoichiometric compound the zero of energy is set to the valence band maximum, while for the doped compound the zero of energy is set to the zero-temperature Fermi energy.

all describe planar transport, and describe relatively dispersive electron bands (compared with the very flat L–H band).

This dispersion causes a relatively large $\sigma(E)$ at these points, as since $\sigma(E) = N(E)v^2(E)\tau(E)$, with $N(E) \propto 1/v$ we find a large $\sigma(E)$ due to the dispersion in these directions. Note that it is the flat L–H band that is responsible for the high thermopower and that a mixture of heavy and light bands has previously been shown to be favorable for thermoelectric performance [26]. However, no such mixture of heavy and light conduction bands is present for $c$-axis transport, represented in these figures as $\Gamma$ – A and L–M—there is no relevant $\Gamma$–A pocket and L–M is only mildly dispersive. By contrast L–M is more dispersive in the valence band, and as shown in figure 1 there is in addition a dispersive valence band along the $\Gamma$–A direction. This is borne out in by the low-temperature planar and $c$-axis $\sigma/\tau$ (i.e. $N(E)v^2(E)$) results presented in figure 5. As the figure depicts, the $c$-axis values in the conduction band are very small in the first quarter eV above the conduction band minimum, while that just below the valence band maximum rises very steeply.

Given this result, one might then ask about the hole-doped $c$-axis thermopower, since the transport function (whose low temperature slope is proportional to the thermopower) rises very steeply above the VBM. We depict this (at 1250 K) in figure 6. Indeed, the $c$-axis thermopower is large (above 200 $\mu$V K$^{-1}$) at low dopings, although this does not persist to the large carrier concentrations of $3 \times 10^{21}$ cm$^{-3}$ for which it persists for the electron-doped case. The reason for this difference is the lack of a heavy mass band in the valence band, as is present in the conduction band. There is still some potential for good thermoelectric performance for hole-doped materials, however, because the conductivity at these heavy dopings (not shown) is roughly three times larger in the $c$-axis direction. In this case the $c$-axis thermopower will
Figure 5. The calculated transport function $N v^2$ at low temperature as a function of chemical potential. Note the small slope of this function in the first 0.25 eV in the conduction band $c$-axis direction and the large $c$-axis slope in the valence band.

Figure 6. The calculated hole-doped thermopower at 1250 K.

predominate, leading to an actual 1250 K thermopower in a polycrystalline sample of roughly 180 $\mu$V K$^{-1}$ for a doping of 0.2 holes per unit cell. Depending upon actual mobility values this may yield good performance (ZTs near unity).

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3. Discussion and conclusion

The thermopower results of the previous section suggest that the narrow band gap semiconductor may show excellent high-temperature performance between 900 and 1250 K at heavy electron dopings of $2-4 \times 10^{21} \text{cm}^{-3}$, and potentially good performance for hole dopings of $2 \times 10^{21} \text{cm}^{-3}$. Note that alloying, perhaps with Sn on the Si site, may be necessary to reduce the lattice thermal conductivity and thereby achieve optimal performance. However, there is an unknown—the mobility at these dopings—which could complicate this conclusion.

CrSi$_2$ ordinarily forms as a degenerate p-type semiconductor, [14, 15, 32, 33], and it is only relatively recently that n-type samples have been developed [34]. The paper of Nishida and Sakata [35] suggests that electron mobility may be as low as one hundred times lower than hole mobility, but this appears to be unlikely given the relative similarity of the hole and electron masses as presented in figure 1. The n-type samples of [34] showed a room temperature mobility of $12 \text{cm}^2/(\text{V s})$ at room temperature at a carrier concentration $n = 1.2 \times 10^{21} \text{cm}^{-3}$. If this mobility is assumed to follow a $1/T$ law, it would have the value $3 \text{cm}^2/(\text{V s})$ at 1250 K and at heavy dopings of $3 \times 10^{21} \text{cm}^{-3}$ would yield a conductivity of order $1000 \Omega^{-1} \text{cm}^{-1}$. This would then yield an electronic thermal conductivity of roughly $3 \text{W/(m K)}$, or probably somewhat larger than the lattice term at this temperature. Figures-of-merit $ZT$ at or exceeding unity might then result, with the actual value depending on experimental values of the mobility.

With regards to doping, the heavy dopings assumed here should be readily achievable. While heavy d-bands, as pictured here, are not always straightforward to dope, as mentioned above n-type films [34] have already been synthesized via ion implantation with electron concentrations $n$ in the relevant range. Furthermore, the narrow band gap suggests that both heavy n-type and p-type doping should be possible.

One possibility that could be explored to achieve heavy electron doping would be the insertion of a light filler atom such as lithium into the tetrahedral site. Such an electropositive element can be expected to readily donate its lone valence electron to the conduction band; its nearest neighbor distance with Si would be 1.66 Å, a reasonable value for these two small atoms. Another possibility is phosphorus doping on the Si site, as has previously been used to dope pure Si. Since the relevant bands are nearly all Cr character, this may have less of a mobility reduction than doping on the Cr site would produce.

We note also that oxidation in air is an issue at the elevated temperatures described here, as detailed in [36], so that efforts to isolate the sample from air may be necessary for experimental investigations. One further issue is that of magnetism; as one might expect there is a rather large density of states in the conduction band and there is therefore the possibility of a magnetic instability at these heavy dopings. We have performed spin-polarized calculations within the virtual crystal approximation to check this (at a doping of 0.3 electrons per unit cell) and indeed find an instability, but a very marginal one with magnetic moment $0.1 \mu_\text{B} \text{Cr}^{-1}$ atom and an ordering energy of order 1 meV Cr$^{-1}$. Such an instability is not likely to be relevant for transport at the elevated temperatures studied here. We also note that the 1250 K conditions envisioned in this work are still well below the 1711 K melting point of this compound. Regarding the stability of the ground state calculated electronic structure at the elevated temperatures modeled here, previous calculations [20] demonstrate a band gap which decreases with uniaxial (i.e. $c$-axis) pressure, suggesting that the band gap may increase due to thermal expansion at elevated temperatures. This would reduce bipolar conduction and suggests that our high temperature thermopower may be understated. Finally, CrSi$_2$ is composed of inexpensive,
non-toxic, abundant elements and thus may be suitable for large-scale high-temperature applications such as thermoelectric generators.

To summarize, in this paper we have presented first principles calculations suggesting that heavily electron-doped CrSi$_2$ may show excellent thermoelectric performance at elevated temperatures around 1250 K.

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