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## Titanium forms a resonant level in the conduction band of PbTe

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### Abstract

Titanium is a donor in PbTe, leading to electron concentrations up to  $n \sim 1 \times 10^{19} \text{ cm}^{-3}$ , above which it pins the Fermi level at about 52 meV above the conduction band edge. While Ti is thus a resonant level, it does not enhance the thermopower above that of similarly-doped PbTe, suggesting that the electrons on Ti are localized. Delocalized electrons appear again when the Ti concentration is increased so that  $1 \times 10^{19} \text{ cm}^{-3} < n < 1 \times 10^{20} \text{ cm}^{-3}$ , suggesting the appearance of impurity band conduction. The PbTe:Ti system is analogous to the well-studied HgSe:Fe system. A model for Fermi level pinning is proposed that is based on the chemical equilibrium between different ionization states of the donor impurity.

## Introduction

Resonant impurity levels have been shown to be capable of enhancing the thermopower  $S$  and thus the thermoelectric figure of merit  $zT$  of important thermoelectric semiconductors such as  $p$ -type PbTe<sup>1</sup> and Bi<sub>2</sub>Te<sub>3</sub><sup>2</sup>. The quest here was for a resonant level in the conduction band of PbTe, and hints existed in the literature<sup>3</sup> that Ti could be one. In this paper, we describe the MBE growth of Ti-doped PbTe and its electronic transport properties. Ti in PbTe shows Fermi level pinning characteristics very similar to those of Fe in HgSe.<sup>4</sup> The main observation in the latter system is that the concentration of free electrons,  $n$ , increases with increasing the iron concentration  $N_{Fe}$ , until  $n \sim 4.5 \times 10^{18} \text{ cm}^{-3}$ ; above that concentration labeled  $N_{FeCrit}$ , adding Fe has no effect. The model is that Fe forms a resonant level about 210 meV above the conduction band edge. Since Fe substitutes for Hg, its “neutral” valence is Fe<sup>2+</sup>, Fe<sup>3+</sup> acts as a donor. For  $N_{Fe} < N_{FeCrit}$ , iron goes in as Fe<sup>3+</sup>+1e<sup>-</sup>. When  $N_{Fe} > N_{FeCrit}$ , any  $N_{Fe}$  in excess of  $N_{FeCrit}$  goes in as Fe<sup>2+</sup>.

Here a similar action is suggested to be at work for Ti in PbTe. It is reasonable to assume that Ti substitutes for Pb, and is neutral in its Ti<sup>2+</sup> state. The hypothetical donor state would then be either Ti<sup>3+</sup> + 1e<sup>-</sup>, as suggested by Sisov et al.<sup>3</sup>, or Ti<sup>4+</sup> + 2e<sup>-</sup> since Ti<sup>4+</sup> is more frequently encountered in chemical compounds. The Hall effect is measured up to 460 K, and in some samples to 580K, and is temperature-independent. In the more heavily doped samples the mobility displays an unusual temperature dependence. In short, excess electrons are observed by Hall effect measurements in concentrations increasing with increasing  $N_{Ti}$  up to  $n = n_{Crit} = 1 \times 10^{19} \text{ cm}^{-3}$ . Samples with higher  $N_{Ti}$  have a constant electron concentration of  $n_{Crit}$ , but at the highest values of  $N_{Ti}$  free electrons appear again in the Hall effect measurements. We suggest that Ti induces a resonant

level at an energy of about 52 meV above the conduction band minimum, which is the value where the Fermi level at 0 K is in the undistorted conduction band of pure PbTe for  $n=n_{Crit}$ . A model for Fermi level pinning is proposed for either PbTe:Ti or HgSe:Fe systems, based on the equations originally developed for chemical buffers and adapted here to semiconductor physics.

No excess thermopower is shown over the value that similarly-doped PbTe would have, i.e. the thermopower,  $S$ , of the Ti-doped samples falls on the  $S(n)$  “Pisarenko” relation for the conduction band of pure PbTe, suggesting that electrons on Ti atoms in excess of  $N_{Crit}$  are localized and contribute to neither thermopower nor Hall effect. The fact that new free electrons appear in the Hall effect and resistivity measurements at the highest Ti concentration, up to  $n\sim 10^{20}\text{ cm}^{-3}$  suggests that for a second critical value of  $N_{Ti}$  an impurity band may appear where the Ti wavefunctions overlap each-other and the electron on Ti delocalize again. Transport data in this regime are presented.

## **Experiments**

The investigated samples were grown using an EPI930 molecular beam epitaxy (MBE) system. Before the growth  $10\times 10\times 25\text{ mm}^3$  and  $12\times 12\times 25\text{ mm}^3$  BaF<sub>2</sub> single crystals are cleaved into  $\sim 1\text{ mm}$  thick substrates with an  $\langle 111 \rangle$  oriented surface. The substrates were mounted to the Mo-substrate holder using an InGa eutectic. In order to remove water from the substrate surface, the substrates are heated up to 180°C for 18 minutes in the intro chamber. An additional thermal cleaning step (425 °C for 25 minutes) was done in the growth chamber. Then the substrates were cooled down to growth temperature of 350°C (thermocouple reading). The growth chamber is equipped with a PbTe compound effusion cell, a Te effusion cell for chalcogen stabilization and a

Ti high temperature effusion cell for doping. The growth rate was chosen to be 1.25 $\mu\text{m}$  per hour with a PbTe:Te flux ratio of 10:1. The fluxes were determined using an ion gauge. The Ti-cell temperature was changed from 1250 $^{\circ}\text{C}$  up to 1500 $^{\circ}\text{C}$ . The film thickness was chosen as 2 $\mu\text{m}$  and measured after the growth using scanning electron microscopy (SEM) on cleaved samples with a measurement error of around 10%. The sample thickness of selected samples were crosschecked using Fourier transformation mid infrared (FTIR) spectroscopy (not shown here) yielding in a good agreement with SEM results.

At room temperature, the thermoelectric properties of each thin film are investigated in a simple thermopower ( $S$ , or Seebeck coefficient) measurement setup. During the measurement a temperature gradient of 10 K was applied to generate the Seebeck voltage which is detected simultaneously with the exact temperature difference using two thermocouples. Hall effect measurements using the van-der-Pauw method were used to determine the electrical conductivity, carrier concentration and mobility. For all these room temperature measurements, the samples were electrically connected using Au plated spring contacts. On selected samples the electrical contacts were realized by gold wires soldered onto the corners of the samples using In-solder. Both contacts showed ohmic behaviour. During the measurement electrical currents in the region of  $\pm 5\text{mA}$  and magnetic fields of  $\pm 0.2$  Tesla were used. N-type conduction was observed in all Ti doped PbTe samples while the undoped PbTe samples showed p-type conduction and free carrier concentrations of around  $\sim 3 \cdot 10^{17} \text{ cm}^{-3}$ . Fig 1 shows the dependence of the free electron concentration on the Ti cell temperature. The Ti flux being an exponential of that temperature, and assuming that the Ti sticking ratio is concentration-independent,

the Ti cell temperature is thus proportional to the logarithm of  $N_{Ti}$ , the concentration of Ti atoms in the films.

The temperature dependent electrical conductivity and Seebeck-coefficients were measured in two different setups. From room temperature to 320°C (600K) an Fraunhofer IPM-SRX setup was used with a sample holder after Boffoué & al.<sup>5</sup> A temperature gradient up to 3K is set on the sample through two small heaters. Two thermocouples measure the generated voltage and the temperature gradient continuously. The same thermocouples are used to determine the voltage drop in a 4 point electrical conductivity measurement. A few selected samples were measured from 78 K to 620 K in a flow cryostat in an electromagnet (-1.4T<H<1.4T), and resistivity, Hall, Seebeck and Nernst coefficients were measured. Contacts were made using gold-filled epoxy. Seebeck coefficient ( $S$ ) and transverse adiabatic Nernst-Ettingshausen coefficient were measured using the DC static heater and sink method. The isothermal Nernst coefficient  $N$  could be calculated from the adiabatic one using a correction factor as described by Tsdil'kovskii,<sup>6</sup> but, because heat conduction was dominated by the substrate, the correction factor was negligibly small. The electrical resistivity ( $\rho$ ) and Hall coefficient ( $R_H$ ) were measured using an AC bridge in a 4-wire configuration. We define  $N$  and  $R_H$  as the low magnetic-field slopes of the transverse Nernst voltages and Hall resistances, respectively. No second carrier was detected in the Hall voltages. For thermometry, type T thermocouples were used, with 25  $\mu\text{m}$  wires to minimize heat losses. Errors on  $S$  are of the order of  $\sim 3\%$ ; errors on  $N$ ,  $R_H$ , and  $\rho$  are dominated by inaccuracies in measurements of sample geometry, and we estimate them to be  $\sim 5\%$  on  $N$  and  $R_H$ , and  $\sim 7\%$  for  $\rho$ . The results are presented and discussed in the next section.

## Discussion

The log-log plot of  $n$  versus  $N_{Ti}$  shown in Fig. 1 has the same shape as that for Fe in HgSe<sup>4</sup>, and illustrates Fermi level pinning. We suggest the following model already outlined in the introduction, and represented schematically in the insert of Fig. 1.

Assuming that Ti substitutes for Pb, which is essentially divalent in PbTe, its electrically neutral state is Ti<sup>2+</sup>. Either Ti<sup>3+</sup> or Ti<sup>4+</sup> can then be assumed to be a donor, following a chemical equation:  $Ti^{2+} \leftrightarrow Ti^{(2+k)+} + k e^-$ , with  $k=1$  for Ti<sup>3+</sup> or  $k=2$  for Ti<sup>4+</sup>. This indeed is the case as long as  $N_{Ti} < N_{TiCrit}$ , some critical value. Assuming that the Ti level is set at an energy  $E_{Ti}$  above the conduction band edge, then when  $N_{Ti}$  is such that the Fermi level reaches  $E_F = E_{Ti}$ , electrons on excess Ti atoms remain localized on them. Additional Ti atoms are then no longer (2+k)-valent (tetra- or trivalent) but divalent, and thus neutral in the lattice. In this image,  $N_{TiCrit}$  is reached when  $n = n(E_F = E_{Ti})$ . Solving this condition using the conduction band parameters of PbTe, we obtain  $E_{Ti} \sim 52$  meV at room temperature.

This picture can be quantified with a model based on adjusting the chemical equilibrium equations valid for buffer solutions to the ionization of impurities in semiconductors, which can be applied for both Ti in PbTe and  $Fe^{2+} \leftrightarrow Fe^{3+} + e^-$  in HgSe, generally written as:



where  $k=1$  for  $M=Fe$  in HgSe and  $k=2$  or  $1$  for  $M=Ti$  in PbTe. The ionization energy  $E_{Ti}$  in Fig. 1 is generalized to  $E_D$  for the sake of the following model.

In the low doping region (left in the insert of Fig. 1), the electron bound states have higher energy than the free electrons, therefore, impurities are fully ionized to

$M^{(2+k)+}$  and contribute to the increase of electron concentration, and electron concentration increases linearly with doping level as  $n=k \cdot N_M$ . However, as  $E_F$  increases, and the difference between free electron and bound electrons become smaller, the impurities becomes partly de-ionized from their  $M^{(2+k)+}$  state to “neutral”  $M^{2+}$ . Because the bound electrons are not measured by Hall effect, the free electron concentration shows a flat region. As the doping level further increases, the bound states on  $M$  begin to overlap, and form impurity bands. Once they become mobile electrons instead of bound electrons, they contribute to the Hall effect and the carrier concentration rises again.

The Gibbs free energy change in reaction (1) is the ionization energy plus, for the case where  $k=1$ , the Gibbs free energy of the electron, i.e. the Fermi energy minus the electron affinity:  $\Delta g_0 = o(M^{3+}) - o(M^{2+}) + o(e^-) = o_i + E_F - \chi$ . The case where  $k=2$  is more subtle, but can be simplified by considering the electron pair with a binding energy  $E_p$  as the product of the reaction; this can be generalized to a  $k$ -electron quasi-particle of binding energy  $E_p$ . The Gibbs free energy now becomes the impurity ionization energy plus the Fermi energy plus the quasi-particle binding energy, and minus the electron affinity. The more general case can now be written as

$$\Delta g_0 = o(M^{(2+k)+}) - o(M^{2+}) + o(ke^-) = o_i + E_F + E_p - \chi \quad (2),$$

where  $E_p$  is zero when  $k=1$ .

Reaction (1) has an equilibrium constant  $K$  which is given ( $N_a$ = concentration of anions in the matrix) by:

$$\exp\left(-\frac{\Delta g_0}{k_B T}\right) \equiv K = \frac{\frac{N_{M^{(2+k)+}}}{N_a} \cdot \left(\frac{n}{N_a}\right)^k}{\frac{N_{M^{2+}}}{N_a}} = \frac{N_{M^{(2+k)+}} n^k}{N_{M^{2+}} N_a^k} \quad (3).$$



Labeling now the total concentration of dopant atoms  $N_M = N_{M^{2+}} + N_{M^{(2+k)+}}$ , Fermi-

Dirac statistics give the relations:

$$\frac{N_{M^{2+}}}{N_M} = \frac{1}{1 + \exp\left(\frac{E_D - E_F}{k_B T}\right)}; \frac{N_{M^{(2+k)+}}}{N_M} = 1 - \frac{1}{1 + \exp\left(\frac{E_D - E_F}{k_B T}\right)} \quad (4).$$

$$\frac{N_{M^{(2+k)+}}}{N_{M^{2+}}} = \exp\left(\frac{E_D - E_F}{k_B T}\right)$$

Combining (2-4) yields the governing equation for Fermi level pinning:

$$\exp\left(-\frac{o_i + E_F + E_p - \chi}{k_B T}\right) = \left(\frac{n}{N_a}\right)^k \exp\left(\frac{E_D - E_F}{k_B T}\right) \quad (5)$$

$$n = N_a \exp\left(-\frac{o_i + E_p - \chi + E_D}{k(k_B T)}\right)$$

where the number of free electrons does not vary with number of dopant impurities, but only with the ionization properties of the impurity and its energy level (and  $E_p$  if  $k > 1$ ). Equation (5) does depend on the valence of the donor impurity,  $k$ , but the pinning action is present whether  $k=1$  or 2. For  $k > 1$ ,  $E_F$  refers to Fermi energy of the  $k$  electrons treated as a whole quasi-particle both in the ionization reaction (2) and in the Fermi-Dirac distribution (4). Equation (5) holds when the doping impurity is of specie  $M$  (self-pinning) or, in the case of double-doping, of another specie, which is what a chemical buffer does.

The electrons that are pinned on the  $Ti^{2+}$  atoms are likely localized on their  $3d$  levels where they do not contribute to Hall-effect or resistivity measurements. The behavior of samples grown with a Ti cell temperature in excess of  $1450^\circ C$  show an additional free carrier concentration, although these should still be included in (5): these additional free carriers are likely to still reside on  $Ti-3d$  states, which, at these high

concentrations, now become delocalized and form an impurity band in which charge can be transported.

Turning now to the temperature-dependent results for the various transport properties measured, Fig. 2 shows the electrical conductivity and Fig. 3 the free carrier concentration for Hall-effect, calculated assuming  $n=(e R_H)^{-1}$ ; this latter quantity does not substantially depend on temperature, which indicates that the temperature-dependence in Fig. 2 is all due to mobility effects; the latter is shown in Fig. 4. The low-temperature mobilities are quite good. A comparison with a  $T^{5/2}$  power law indicates that low-doped samples may tend to it asymptotically, but higher-doped samples not.

The temperature-dependent thermopower is shown in Fig. 5. A Pisarenko plot of the thermopower at 300K versus free electron concentration is shown in Fig. 6, and the data fall accurately on top of the line that can be calculated using the known conduction band parameters of PbTe and assuming mostly acoustic phonon scattering. In contrast to the case of Tl in PbTe, where the presence of the resonant Tl level strongly enhances the thermopower above the Pisarenko relations, no enhancement is observed here at room temperature, which does not exclude the eventual presence of resonant scattering at cryogenic temperatures, as had been suggested earlier.<sup>3</sup> Indeed, resonant levels are known to increase  $S$  at a given carrier concentration through two effects.<sup>7</sup> The first effect is the increase of the density-of-states (DOS)  $g(E)$  at the Fermi energy, and the second is “resonant scattering”, a strong increase in the energy dependence of the mobility when the Fermi energy is near the resonance energy. Indeed, the energy-dependent thermopower in degenerate statistics is given by the Mott formula which can be decomposed and written as:<sup>7</sup>

$$S = \frac{\pi^2}{3} \frac{k_B}{q} (k_B T) \left( \frac{g(E)}{n(E)} + \frac{d \ln \mu(E)}{dE} \right)_{E=E_F} \quad (6),$$

where the first term is the contribution of the DOS, and the second gives rise to resonant scattering. Because phonon scattering dominates at higher temperatures, the resonant scattering term is only observed at cryogenic temperatures, if at all.

This major difference between the Ti:PbTe and the Tl:PbTe cases is, in fact, consistent with the behavior of the Hall data in Fig. 1. Localized electrons on Ti  $3d$ -levels do not contribute to either the Hall or Seebeck effects, in contrast to those on the Sn level in  $\text{Bi}_2\text{Te}_3$  or the Tl level in PbTe; they might, however, still resonantly scatter the band electrons of the PbTe host at cryogenic temperature. The Tl levels in PbTe are known to be due to  $6s$ -Tl levels coupled with neighboring Te  $p$ -electrons.<sup>8</sup> Note that in references [1] and [2], data are shown on the Pisarenko plot are plotted for different hole concentrations, which implies *ipso facto* that these holes were mobile enough to contribute to the Hall and thus Seebeck coefficients. By the same reasoning, Tl in PbTe and Sn in  $\text{Bi}_2\text{Te}_3$  do not show Fermi-level self-pinning, although the Tl level in PbTe does pin holes that come from double-doping.<sup>9</sup> This implies that no enhancement in thermopower should be expected at room temperature when the Fermi level is pinned as shown in Fig 1, although the resonant scattering contribution may be present at low temperature.

The transverse Nernst-Ettingshausen coefficient is shown in Fig. 7. The low negative value observed on most samples is indicative of dominantly acoustic phonon scattering. The large positive value observed on the sample with a pinned Fermi level is striking: while it may point to strong ionized impurity scattering, it is not clear why that happens only at an intermediate Ti concentration. For completion, we show the

thermoelectric power factor ( $S^2\sigma$ ) in Fig. 8; it does not show any enhancement over that of conventionally doped  $n$ -type PbTe.

### **Summary**

In conclusion, Ti is a resonant level with an energy approximately 52 meV in the conduction band of PbTe. It displays Fermi level pinning behavior, quite similarly to Fe in HgSe. A model is developed that explains the origin of Fermi level pinning in terms of an equilibrium constant between different ionization states of the Ti in the PbTe lattice. As the pinned electrons are in localized  $3d$  states on Ti, they do not contribute to conduction or to thermopower, and no enhancement in the thermopower or power factor is observed.

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## Figure Captions

Fig. 1 Hall-effect free electron concentration at 300 K as a function of Ti-cell temperature, which scales with the logarithm of  $N_{Ti}$ .

Fig. 2 Temperature dependence of the electrical conductivity at high and low temperatures. ( $T(Ti)$ : Temperature of the Ti effusion cell in °C)

Fig. 3 Temperature-dependence of the free electron concentration measured by Hall effect.

Fig. 4 Temperature-dependent mobility of PbTe:Ti. A comparison with a  $T^{5/2}$  power law is made.

Fig. 5 Temperature-dependent thermopower of PbTe:Ti. ( $T(Ti)$ : Temperature of the Ti effusion cell in °C)

Fig. 6 Pisarenko plot of thermopower versus electron concentration at 300 K. No anomaly is observed when the data of PbTe:Ti are compared with conventionally-doped material.

Fig. 7 Isothermal transverse Nernst-Ettingshausen coefficient versus temperature at low temperatures.

Fig. 8 Thermoelectric power factor of PbTe:Ti. ( $T(Ti)$ : Temperature of the Ti effusion cell in °C)

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- <sup>9</sup> S. A. Nemyov, Yu. I. Ravich, Phys. Usp. **41**, 735 (1998). Fermi level pinning in the case of double-doping is very different from that presented here. Consider the case of a PbTe sample double-doped with a fixed concentration  $N_{Tl}$  of thallium atoms and a variable concentration  $N_{Na}$  of sodium atoms, both acceptors. When  $N_{Na} > N_{Tl}$ , the concentration  $n$  of free holes increases with  $N_{Na}$ , but when  $N_{Na} < N_{Tl}$ , it does not: presumably every pair

of holes that comes from two Na atoms change the valence of the TI from  $Ti^{1+}$  to  $Ti^{3+}$  rather than filling extended states that contribute to the Hall measurements.

Figure 1

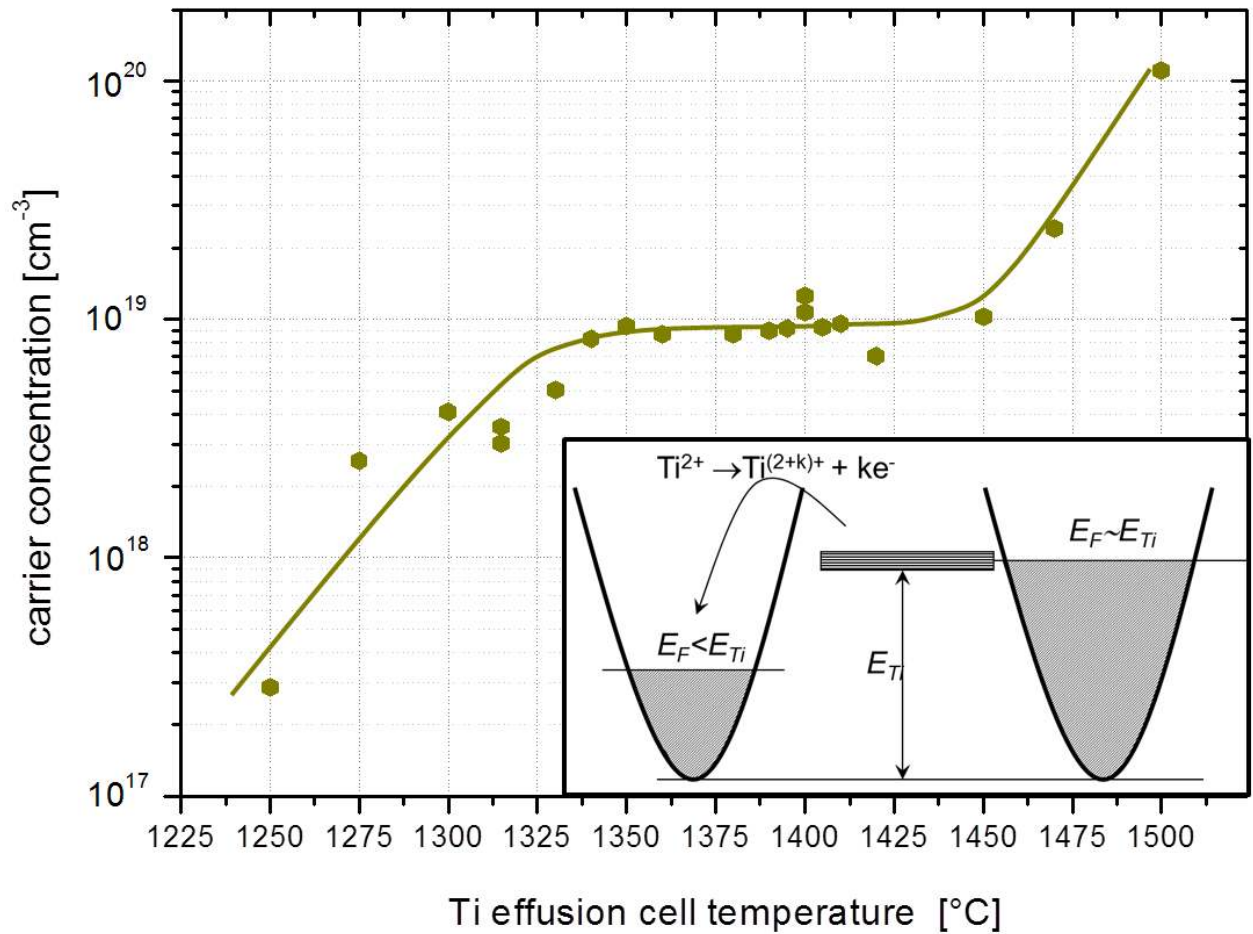


Figure 2

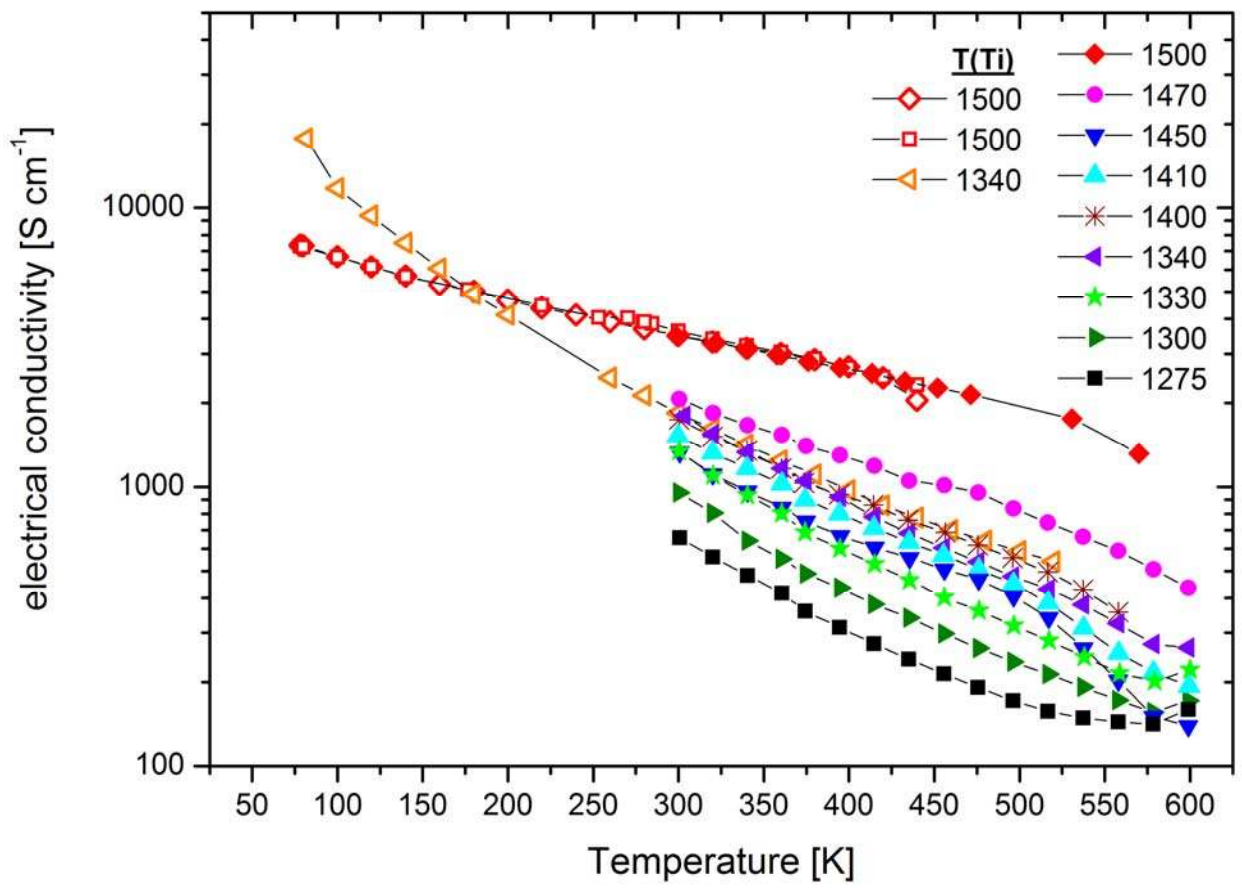




Figure 3

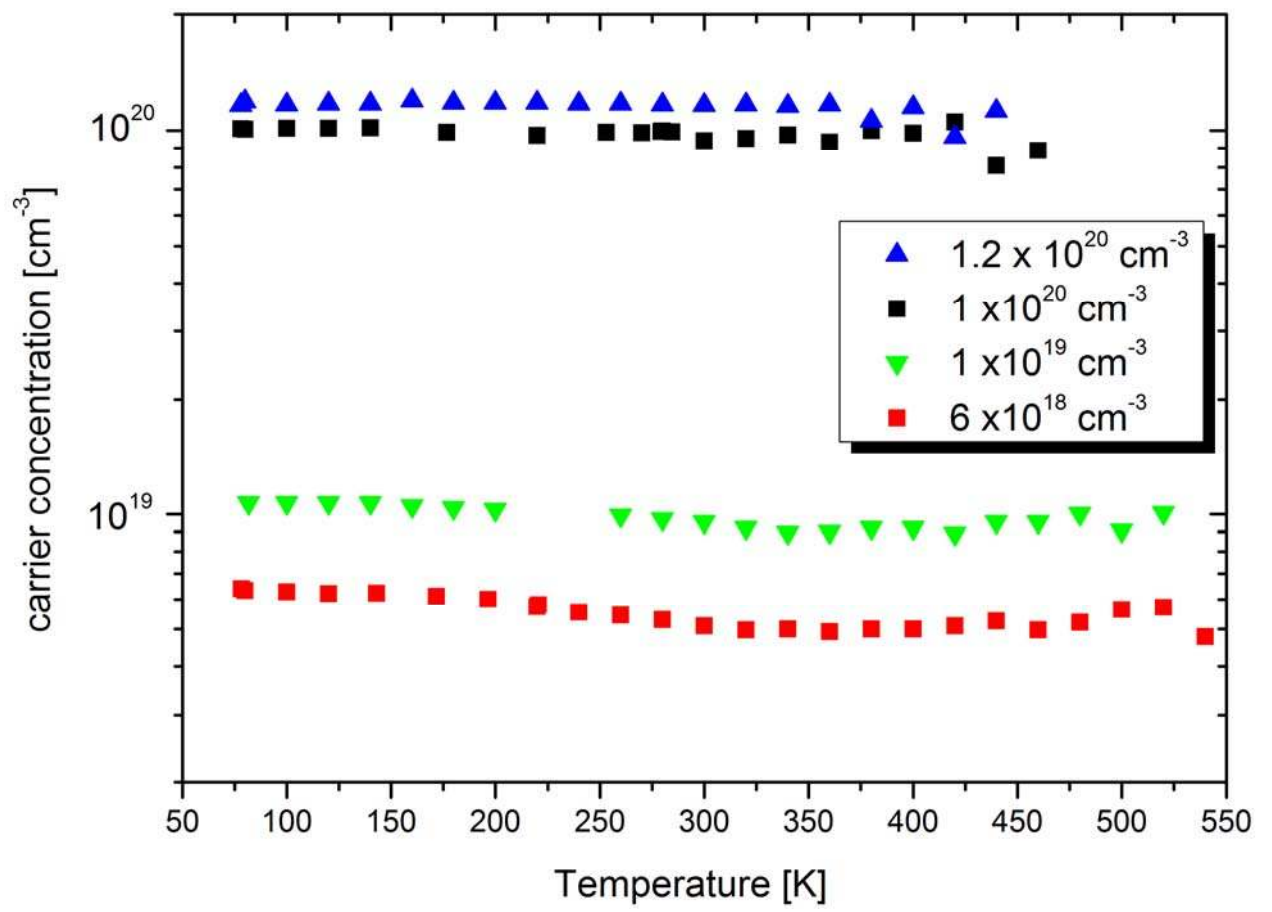


Figure 4

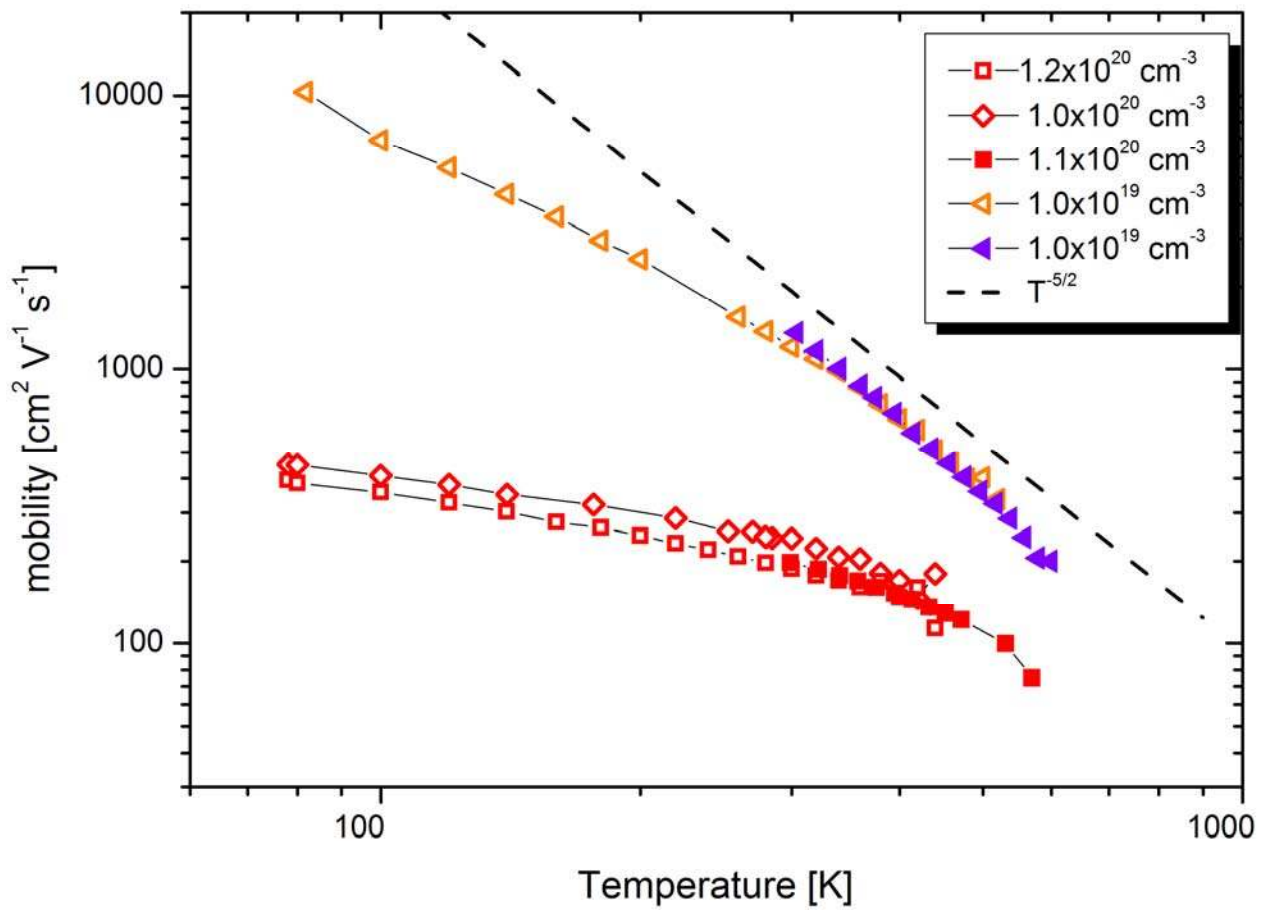


Figure 5

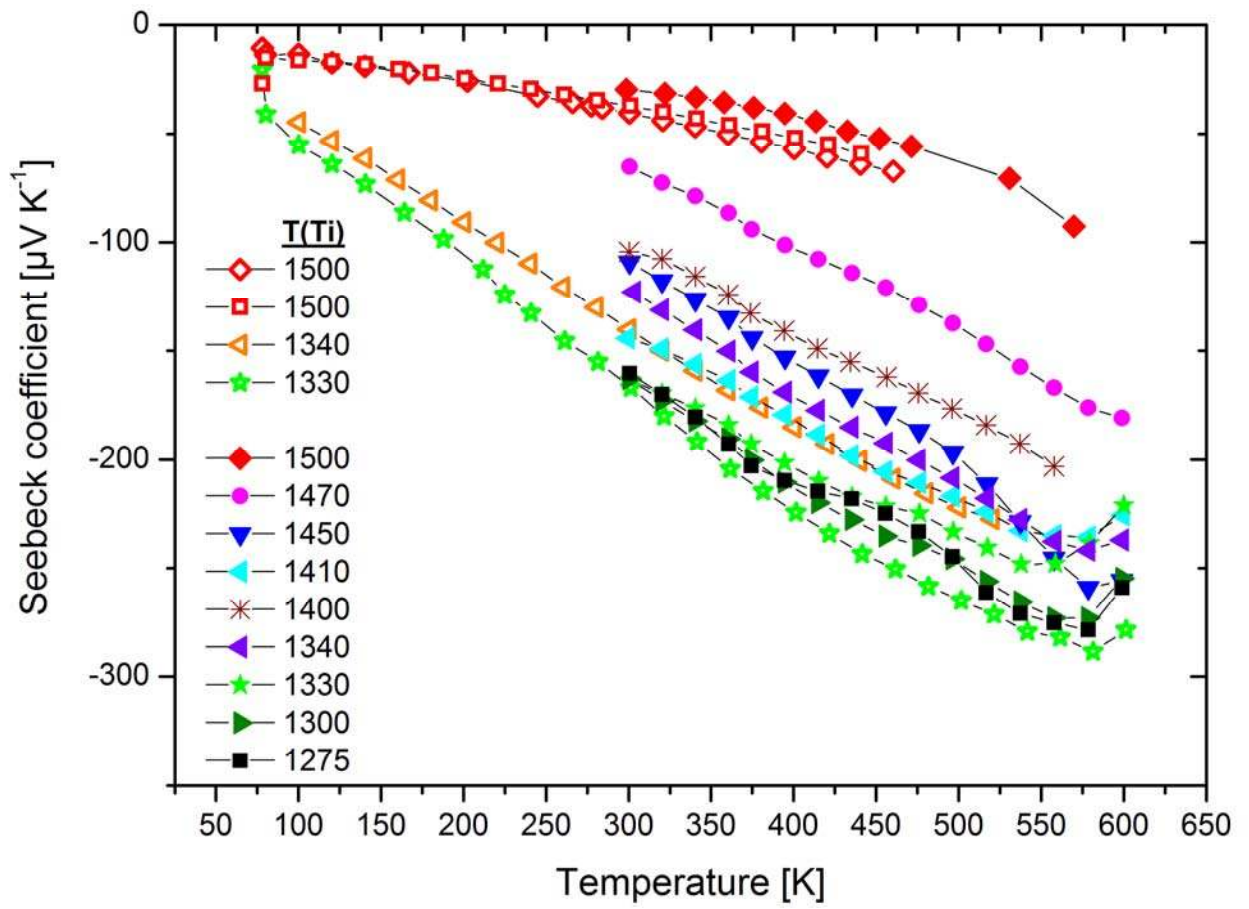


Figure 6

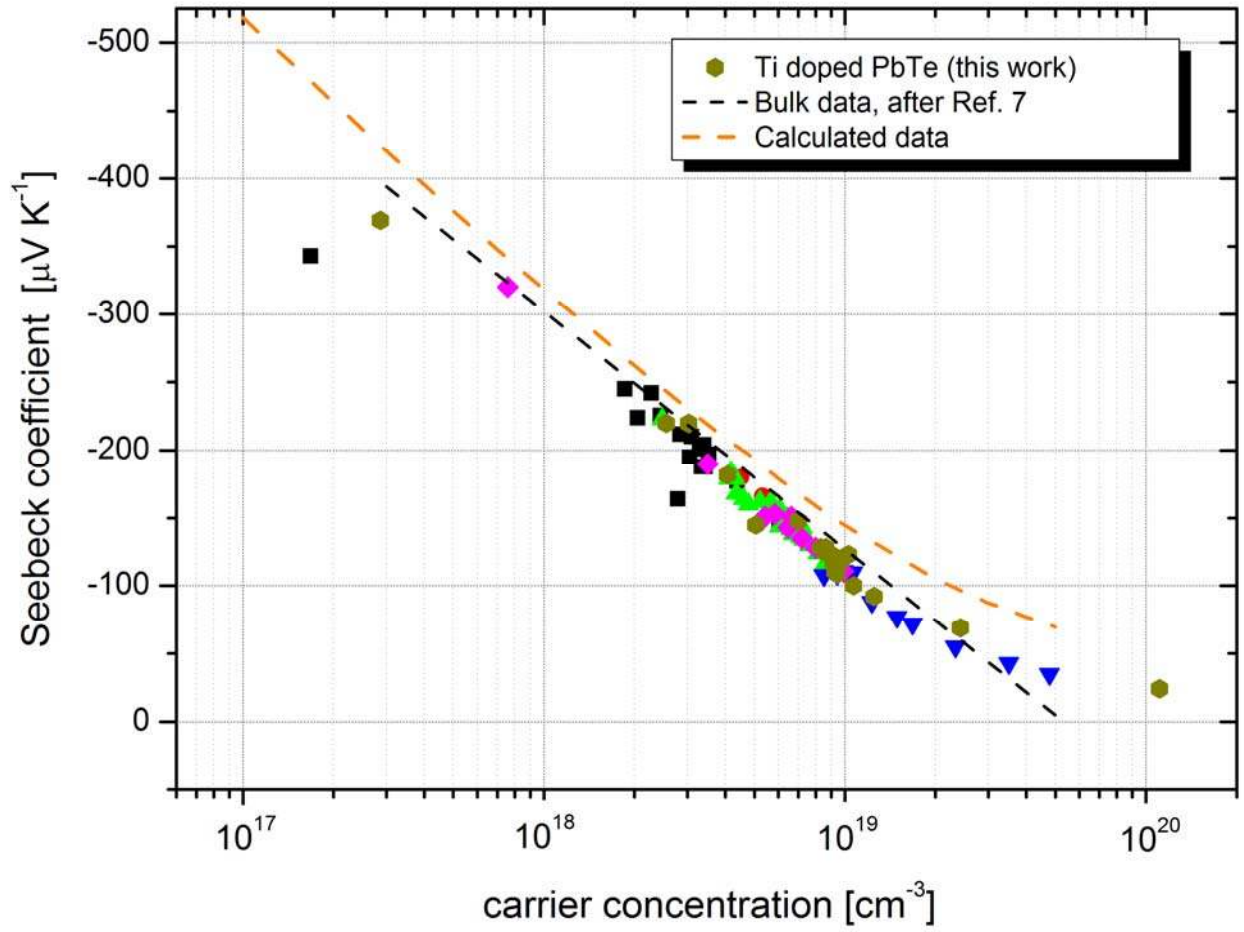


Figure 7

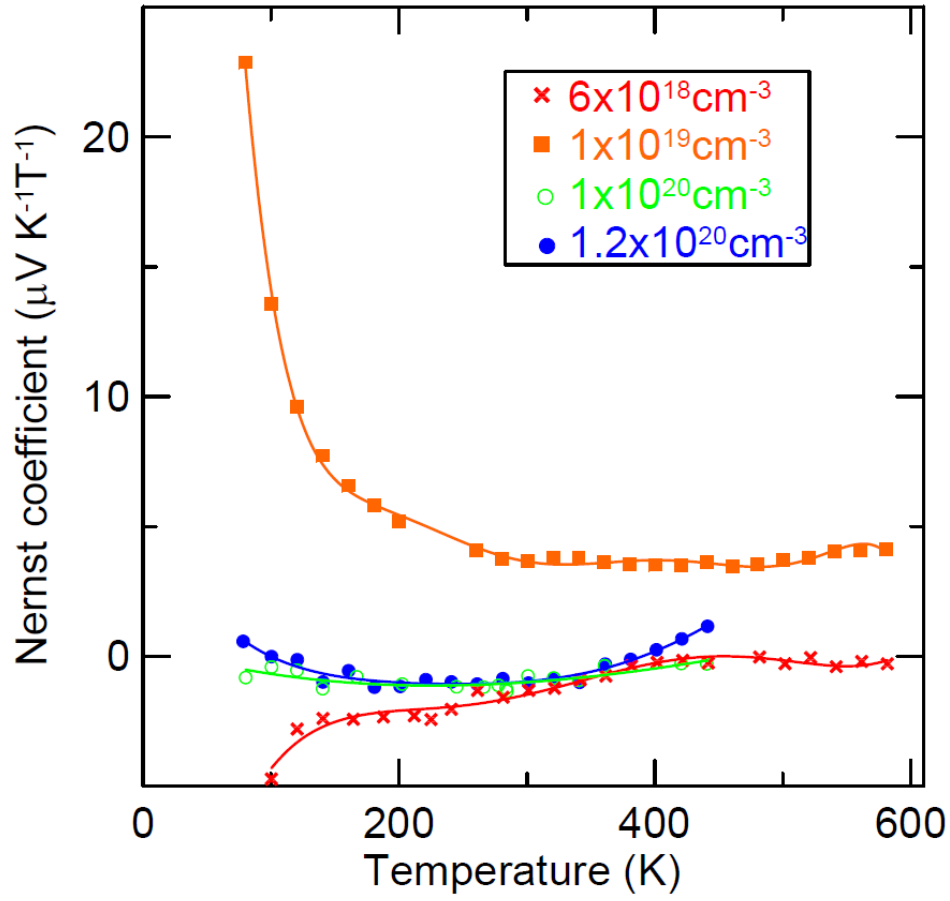


Figure 8

