Significant suppression of thermal conductivity in FeSb$_2$ by Te doping

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Kondo insulator like material FeSb$_2$ was found to exhibit colossal Seebeck coefficient. It would have had huge potential in thermoelectric applications in cryogenic temperature range if it had not been for the large thermal conductivity. Here we studied the influence of Te doping at Sb site on thermal conductivity and thermoelectric effect in high quality single crystals. Surprisingly, only 5% Te doping suppresses thermal conductivity by two orders of magnitude, which may be attributed to the substitution disorder. Te doping also results in transition from a semiconductor to a metal. Consequently thermoelectric figure of merit ($ZT \sim 0.05$) in Fe(Sb$_{0.9}$Te$_{0.1}$)$_2$ at $\sim 100K$ was enhanced by about one order of magnitude when compared to $ZT < 0.005$ in undoped FeSb$_2$.

Fe(Sb$_{1-x}$Te$_x$)$_2$ ($x = 0, 0.005, 0.01, 0.05$) single crystals were grown from excess Sb flux, as described previously. The thermal transport properties including thermal conductivity, Seebeck coefficient, as well as electrical resistivity were measured in Quantum Design PPMS-9 from 2K to 300K using one-heater-two-thermometer method. The direction of heat and electric current transports was along the c-axis of the crystals oriented using a Laue camera. The heat capacity of all samples, which used to derive the phonon mean free path, were measured also using Quantum Design PPMS-9 in the same temperature range.

Figure 1 shows the temperature dependence of the thermal conductivity, Seebeck coefficient and electrical resistivity of samples with different Te doping level. The thermal conductivity $\kappa(T)$ achieves its maximum between 12 and 20K for pure FeSb$_2$, peaking at 250 W/K-m. The Seebeck coefficient changes sign from positive to negative around 120K, indicating presence of two carrier types. The absolute value of $S$ increases rapidly below 40K, and reaches its nearly constant maximum value $|S(T)|_{max} \sim 800 mV/K$ in the temperature interval $20K \sim 10K$. This is similar to previous report. Due to large thermal conductivity, its $ZT$ ($ZT < 0.005$ at 10K) is very low, which seriously limits the realistic applications. A slight substitution of Te at Sb sites (0.5%) significantly suppresses the thermal conductivity by half, i.e., $\kappa_{max} < 90W/K-m$. Further doping with Te induces more significantly decrease in $\kappa$, and only 5% Te doping induces nearly two-order decrease in thermal conductivity. The substitution also induces the significant suppression of the resistivity and a change to metallic ground state. The metallic temperature region increases...
Franz law translated from the electrical resistivity using Wiedemann-Franz law, we have extracted the phonon mean free path. The suppression of thermal conductivity is dominated by the lattice thermal conductivity below room temperature in all investigated crystals especially in the region of large \( S \). We estimated the lattice thermal conductivity \( \kappa_L \) by subtracting \( \kappa_c \) from the total thermal conductivity. By using the kinetic formula \( \kappa_L = \frac{1}{3} \kappa_c \nu l_{\text{phonon}} \) where \( \kappa_c \) is lattice specific heat (Fig.2(a)) and \( \nu \) is the sound velocity, we calculated the phonon mean free path, \( l_{\text{phonon}} \) for three samples with \( x = 0, 0.01, 0.05 \) (Fig.2(b)). The phonon mean free path is suppressed by nearly two orders of magnitude by Te doping. The phonon mean free path is very sensitive to the grain boundary and disorder effect that could enhance the scattering process and suppress the phonon mean free path. The suppression of \( l_{\text{phonon}} \) in our system most likely originates from substitutional disorder in doped crystals in the absence of grain boundaries.

The suppression of thermal conductivity and electrical resistivity by Te doping in FeSb\(_2\) is expected to enhance the thermoelectric figure of merit. Unfortunately, the Seebeck coefficient is suppressed simultaneously with thermal conductivity by Te doping, as shown in Fig.1(b). The peak of \( S(T) \) is also shifts to higher temperature. But it can be expected that for some doping range there is an optimal value of Seebeck coefficient, thermal conductivity and ZT.

Fig.3 (a) shows thermal conductivity of Fe(Sb\(_{0.9}\)Te\(_{0.1}\))\(_2\). It can be concluded that the thermal conductivity is further suppressed. The peak value of \( \kappa \) is only \( \sim 8W/Km \). A maximum of Seebeck coefficient \( \sim 150\mu V/K \) at \( \sim 100K \) is observed, as shown in Fig.3 (b). Correspondingly, the maximum of \( ZT \) achieves 0.04 at about 100K, which is nearly one-order of magnitude larger than \( ZT \sim 0.005 \) at undoped FeSb\(_2\).
In summary, we studied the influence on the thermal conductivity and thermoelectric effect by Te doping at Sb site in FeSb$_2$ single crystal by the self-flux method. Only 5% Te doping induces nearly two-order decrease on thermal conductivity and the phonon mean free path. This may be attributed to substitutional disorder. The Te doping also results in transition from a semiconductor to a metal. Consequently a significantly enhanced thermoelectric figure of merit ($ZT \sim 0.05$) is achieved in Fe(Sb$_{0.9}$Te$_{0.1}$)$_2$ at $\sim 100$K. Even though this value is too small to for applications, our study pointed to a direction for the thermal conductivity suppression in FeSb$_2$.

Note added. We became aware that a preprint was posted on the arXiv.org with similar conclusion on the same day of our submission.

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