Giant magnetothermoelectric figure of merit in Dirac semimetal Cd$_3$As$_2$

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Thermoelectric power of Dirac semimetal Cd$_3$As$_2$ exhibits linear temperature dependence, which is in agreement with the semiclassical Mott’s relation. With increasing magnetic field, the scattering time crosses over from nearly energy independent to linear energy dependent due to the lifting of protection mechanism which suppresses back-scattering. Unlike Fermi liquid systems, enhancement in electrical to thermal conductivity ratio and thermoelectric power with magnetic field, results a giant magneto-thermoelectric figure of merit (2.5 times at 5 T) at room temperature and above.

Dirac [1] and Majorana [2] fermionic excitations in condensed-matter systems not only quench our thirst on fundamental physics but also provide the possibility to manipulate them for technological applications [3, 4]. Recently discovered 3D Dirac semimetal phase in Cd$_3$As$_2$ and Na$_3$Bi is an important member of this family [3, 4]. Similar to graphene [1] and topological insulators [10, 11], it exhibits a linear energy dispersion relation in the bulk and the surface state is topology protected Fermi arc. The major attentions have been focused on the electronic transport properties of Cd$_3$As$_2$ for understanding the nature of band structure [12–16]. The electrical resistivity measurements show that the back-scattering of charge carriers in Cd$_3$As$_2$ is strongly suppressed due to a remarkable protection mechanism [15]. As a result, the mobility becomes very high $\sim 10^7$ cm$^2$ V$^{-1}$ s$^{-1}$. However, the magnetic field lifts this protection mechanism and leads to an unusual giant $H$-linear magnetoresistance. So, it is worthy to study how the lifting of protection mechanism affects the scattering of charge carriers and which relaxation process dominates at high magnetic field. The measurements of resistivity alone is not sufficient to understand the different scattering mechanisms. Thermoelectric power has been used as a powerful tool to probe the relaxation process in metals and semiconductors because it provides complementary information to resistivity.

The materials with high mobility are also considered to be important candidates for studying the thermoelectric properties for the application. Whether a material will be useful in thermoelectric application or not is mainly determined by the figure of merit $ZT$. The material’s parameter $Z$ is defined as $Z=\frac{S^2 \sigma}{\kappa}$, where $S$, $\sigma$ and $\kappa$ are the Seebeck coefficient, electrical conductivity and thermal conductivity, respectively. As $\sigma$ and $S$ are proportional and inversely proportional to the carrier density ($n$), respectively, one cannot enhance the value of $Z$ by considering $n$ only. Unlike $S$, $\sigma$ is also proportional to the mobility ($\mu$) of the charge carrier. This suggests that materials with high mobility but carrier density much less than a good metal can be useful for thermoelectric application. For this reason, semimetals and semiconductors with high mobility such as bismuth-telluride and bismuth-antimony based compounds have been studied extensively [17–24].

Considering the strong response to the magnetic field and the high mobility of Cd$_3$As$_2$, we have pursued a thorough study on thermoelectric properties to probe its possible scattering mechanism and applicability in future technologies. In this Letter, we have shown that $S$ is large and it increases linearly with temperature as in the case of graphene. Like $S$, linear temperature dependence of $ZT$ and its huge enhancement with magnetic field suggest that Cd$_3$As$_2$ may be considered as a potential candidate in thermoelectric application. We have also analyzed the experimental data for understanding the charge scattering mechanism in Cd$_3$As$_2$ both in presence and absence of magnetic field.

Single crystals of Cd$_3$As$_2$ were synthesized by chemical vapor transport technique using polycrystalline Cd$_3$As$_2$ ingot. The one end of the vacuum sealed quartz tube which contains Cd$_3$As$_2$ ingot was maintained at 690°C while the other end was kept at 600°C for 48 h. The furnace was then cooled slowly to room temperature. Several small size shiny plate-like crystals formed at the cold end of the tube were mechanically extracted for transport and magnetic measurements. Powder X-ray diffraction of crashed single crystals shows that these crystals have $I_{41}/acd$ space group and contain no impurity phases. The details are given in supplementary material [25]. The resistivity, thermal conductivity and thermoelectric power (Seebeck coefficient) measurements on Cd$_3$As$_2$ single crystals were done by four-probe technique in a physical property measurement system (Quantum Design). Though several single crystals have been studied, we present the data for a single crystal as a representative. Qualitative similar behavior has been observed for other crystals. In these measurements, the applied magnetic field was perpendicular to the current and temperature gradient.

The temperature dependence of resistivity ($\rho$) of a Cd$_3$As$_2$ single crystal is shown in Fig. 1 (a). Over the entire temperature range 350-2 K, $\rho$ exhibits weakly metallic behavior ($d\rho/dT > 0$). We observe that $\rho$ versus $T^n$ becomes linear for $n$ close to 1.3 as shown in the figure. This behavior of $\rho(T)$ curve is very unusual.
temperature and magnetic field dependence at 300 K and 350 K. For example, the charge carrier. However, the resistivity increases dramatically with the application of magnetic field. The field dependence of $\rho$ is shown in Fig. 1(b) at two different temperatures. We have also done measurements at low temperature and observed qualitative similar behavior. For example, $\rho$ at 2 K increases linearly with field. $\rho$ is observed to increase 24 times at 9 T from its zero field value. Thus, magnetic field strongly enhances the back-scattering of charge carriers.

**FIG. 2.** (Color online) (a) temperature dependence of total thermal conductivity. (b) Magnetic field dependence at 300 K and 350 K up to 9 T.

Figure 2(a) displays the temperature dependence of thermal conductivity of the Cd$_3$As$_2$ single crystal. At room-temperature, the value of $\kappa$ is $\sim$1 W K$^{-1}$ m$^{-1}$ which is comparable to that observed in several thermoelectric materials such as Bi$_2$Te$_3$ and Sb$_2$Te$_3$ [17, 22, 27].

**FIG. 3.** (Color online) (a) Temperature dependence of the thermoelectric power ($S$) up to 350 K. Solid line shows the linear behavior of $S$. (b) Magnetic field dependence of the normalized thermoelectric power at 300 and 350 K up to 9 T where $S(0)$ is the zero-field Seebeck coefficient at the respective temperature.

Figure shows that $\kappa$ is insensitive to $T$ over a wide range. With decreasing $T$, $\kappa$ initially decreases very slowly down to about 50 K and then increases rapidly and reaches a value as large as 10 W K$^{-1}$ m$^{-1}$ at 2 K. Thus, unlike $\sigma$, $\kappa$ shows a sharp increase at low temperature. This is typically phonon dominated region and often, $\kappa$ exhibits a broad peak at low temperature and $T^3$ behavior below this peak due to the boundary scattering of phonons. The absence of such peak down to 2 K implies that the average size of crystallites are larger as compared to phonon mean free path. The effect of magnetic field on $\kappa$ has also been studied. In Fig. 2(b), $\kappa$ has been plotted as a function of field at 300 and 350 K. $\kappa$ decreases very rapidly with increasing field due to the lifting of protection mechanism. Also, $\kappa$ tends to saturate at high field which is expected to be the lattice part of thermal conductivity ($\kappa_L$), as it is independent of the magnetic field. At 300 K, $\kappa$ decreases by a factor of 3 as the magnetic field increases from zero to 7 T, i.e., about 65% reduction in $\kappa$. If we consider the well known equation,

$$\kappa = \kappa_L + \frac{\kappa_e}{1 + \mu_T^2 B^2}$$

(1)

to separate the electronic part ($\kappa_e$) from total thermal conductivity $\kappa$, the $B\to\infty$ limit will give the value of lattice thermal conductivity and $\mu_T$ is the thermal mobility [28]. After fitting the experimental data at 300 K with the above equation, we have found $\kappa_L$=0.41 W K$^{-1}$ m$^{-1}$ which is close to the value of $\kappa$ at 7 T ($\sim$0.50 W K$^{-1}$ m$^{-1}$). If we consider the field dependence of electronic part of thermal conductivity, the reduction is drastic; $\sim$95% at 7 T. Whereas the corresponding reduction in electrical conductivity at this temperature is about 48%. We have also measured the field dependence of $\kappa$ at low temperature but the effect is much weaker as thermal conductivity in this region is dominated by phonon.
nated by electrons. This observation is consistent with the negative sign of the Hall coefficient [12].Remarkably, S shows a linear T dependence over the whole temperature range 2-350 K. It is interesting to compare the T dependence of S of Cd$_3$As$_2$ with that of graphene because of their striking similarities in electronic properties and Cd$_3$As$_2$ is considered as a 3D analogue of graphene. A linear behavior of S(T) has also been reported for graphene [29, 30]. The linear T dependence of S has been ascribed to the Mott formula. For $T < T_F$, where $T_F$ is the Fermi temperature, the well known Mott formula of thermoelectric power is

$$S = \frac{\pi^2}{3e} \frac{T}{\sigma(\varepsilon)} \left. \partial \sigma(\varepsilon) / \partial \varepsilon \right|_{\varepsilon = \mu}$$

(2)

Here $\sigma(\varepsilon)$ is energy dependent conductivity, $\mu$ is the chemical potential and $\mu = E_F$ for $T < T_F$. $\sigma(\varepsilon)$ can be expressed in terms of Fermi velocity ($v_F$), density of states ($D$) and energy dependent scattering time $\tau$; $\sigma(\varepsilon) = \frac{e^2 v_F D(\varepsilon) \tau(\varepsilon)}{2 \pi \hbar^2 v_F^2}$, where $g$ is the total degeneracy. Assuming the energy dependent scattering time $\tau \propto \varepsilon^m$, one gets $S = \frac{\pi^2 k_B}{3e} \frac{k_B T}{E_F} (m + 1)$ for $T < T_F$.

In graphene, it has been shown that the Mott formula holds good up to temperature $T \sim 0.2 T_F$ [29, 30]. For Cd$_3$As$_2$ crystal, we have deduced $E_F \sim 270$ meV using the values of Fermi velocity and Fermi momentum which were calculated from our magnetotransport and magnetization data [32]. The present temperature range of measurement of S is 2-350 K. So, the Mott formula for the thermoelectric power for the Cd$_3$As$_2$ seems to be valid at least up to 0.12$T_F$. As $D(\varepsilon) = \frac{e^2}{2 \pi \hbar^2 v_F}$ for a 3D Dirac system, considering Eq. (2) and the energy-dependent scattering time ($\tau \propto \varepsilon^m$), one gets the expression for thermoelectric power

$$S = \frac{\pi^2 k_B}{3e} \frac{k_B T}{E_F} (m + 1)$$

(3)

We have analyzed the linear T dependence of S using Eq. (3) and deduced $m \sim 0.15$. This implies that $\tau$ is very weakly energy dependent. Though the linear T dependence of S has been predicted for the charged impurity scattering ($m = 2$) and short-range disorder ($m = -2$), here we observe a quite different energy dependence of $\tau$ [33]. However, the present result is consistent with the disorder-induced random mass model for the Dirac fermions where $\tau$ is energy independent [34, 35]. Where as in graphene, the dominant transport mechanism is screened Coulomb scattering from charged impurities [36]. As the zero-field protection mechanism is robust against temperature [12], in Fig. 3(b), we have shown the effect of magnetic field on S at 300 and 350 K as representatives considering application point of view. S increases monotonically with field and tends to saturate at high magnetic field. About 30% increase in S is observed at 5 T. Considering Eq. (3), we observe that $m$ approaches towards 1 i.e., scattering time tends to appear linear energy dependent from nearly energy independent due to the lifting of protection mechanism.

The application potential of a thermoelectric material is mainly determined by the figure of merit $ZT$. In Fig. 4(a), we have plotted the figure of merit as a function of temperature. At low temperature below $\sim 75$ K, $ZT$ is quite small and increases slowly with increasing $T$. This is due to the rapid increase of $\kappa$ at low temperature. However, $ZT$ shows a faster increase with $T$ above 100 K and the dependence is almost linear up to 350 K due to the weak $T$ dependence of $\kappa$ and the approximate linear $T$ dependence of S and $\rho$. At 350 K, $ZT$ reaches $\sim 0.15$. We have deduced $ZT$ up to 300 K for another sample (additional information). For this sample also, $ZT$ is linear in $T$ but the absolute value of $ZT$ is about 15% larger. The power factor ($P$), separated from the total thermal conductivity $\kappa$, is defined as the square of S multiplied by $\sigma$ and plotted in Fig. 4(a). Similar to $ZT$, $P$ shows linear $T$ dependence at high temperature. From the field variation of transport coefficients, we have deduced the magnetic field dependence of $ZT$. In Fig. 4(b), we have plotted the figure of merit as a function of magnetic field at two different temperatures. Figure clearly shows that $ZT$ at 350 K increases almost linearly from 0.15 to 0.38 as magnetic field increases from 0 to 5 T, i.e., 2.5 times increase. This huge increase (150%) in $ZT$ is mainly due to the strong suppression of $\kappa$ and the increase of S with field. The strong suppression of $\kappa$ leads to a large increase ($\sim 50\%$) in $\sigma/\kappa$ ratio at 7 T and as a result a huge enhancement in $ZT$ [29]. This behavior of $\sigma/\kappa$ is very unusual. In most of the systems obeying Fermi liquid behaviour, the ratio $\sigma/\kappa$ at a given temperature remains constant under application of magnetic field. This implies electron loses its energy by inelastic collision with impurities and as a consequence electronic thermal conductivity has stronger field dependence than electrical conductivity. The large value of $ZT$ and its linear increase with temperature and field suggest that Cd$_3$As$_2$ may be considered as a potential candidate for future thermoelectric application.

![FIG. 4. (Color online) (a) Thermoelectric figure of merit (ZT) as a function of temperature (blue symbol) and power factor (P) as a function of magnetic field (black symbol) and (b) magnetic field dependence of ZT at 300 K and 350 K up to 9 T.](image-url)
Now, we compare the observed results on Cd$_3$As$_2$ with the standard thermoelectric material Bi$_2$Te$_3$. Though the values of $P$ and $ZT$ of bulk Bi$_2$Te$_3$ are comparable or slight larger than the corresponding values for Cd$_3$As$_2$ at 350 K, the temperature dependence of these two parameters are very different in two systems. Both $P$ and $ZT$ for Bi$_2$Te$_3$ decrease rapidly with increasing temperature slightly above the room temperature, whereas for Cd$_3$As$_2$ they are still increasing linearly, showing no sign of saturation up to 350 K. If this linear increase of $ZT$ continues up to $200^\circ$C or above, then the value of $ZT$ will be significantly large. Furthermore, several theoretical and experimental research have shown that the application potential of several Bi$_2$Te$_3$-based materials can be enhanced significantly by nanostructuring. For example, it takes more than five decades to enhance $ZT$ value from 1 to 1.4 at $100^\circ$C by nanostructuring, in Bi$_2$-Te$_3$$_{3}$. Appropriate nano inclusion has also shown to enhance the value of $ZT$ of several materials. In both the cases, the lattice thermal conductivity reduces significantly whereas the carrier mobility increases due to filtering of the low mobility carrier. We believe that the values of thermoelectric parameters in Cd$_3$As$_2$ can also be enhanced to reach the practical limit for the application by such kind of sample modifications.

In conclusion, the Seebeck coefficient shows linear temperature dependence over a wide range of temperature, which is in agreement with the Mott’s relation. Analysis reveals that the scattering time evolves from nearly energy independent to linear energy dependent with increasing field, due to the lifting of protection mechanism which suppresses back-scattering. Like $S$, the thermoelectric figure of merit increases linearly with temperature up to 350 K. The strong increase in electrical to thermal conductivity ratio and enhancement of $S$ with magnetic field result a huge increase in $ZT$ at room temperature and above. The large value of $ZT$ and its linear increase with temperature and magnetic field suggest that Cd$_3$As$_2$ may be considered as a potential thermoelectric material for future application by some sample modification.

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Supplementary materials for ” Giant magnetothermoelectric figure of merit in Dirac semimetal Cd$_3$As$_2”.

A. Sample characterization

Phase purity and the structural analysis of the samples were done by high resolution powder x-ray diffraction (XRD) technique (Rigaku, TTRAX II) using Cu-K$_\alpha$ radiation. Figure 5 shows the x-ray diffraction pattern of crashed single crystals of Cd$_3$As$_2$ at room temperature. Within the resolution of XRD, we have not seen any peak due to impurity phase. Using the Rietveld profile refinement program, we have fitted the diffraction pattern and calculated lattice parameters $a=b=12.6440$ Å and $c=25.4472$ Å with space group symmetry $I4_1/acd$.

B. Figure of merit

FIG. 5. (Color online) X-Ray diffraction pattern of powdered single crystals of Cd$_3$As$_2$. In black experimental data, in red the calculated pattern, in blue the difference and in green the Bragg positions.

FIG. 6. (Color online) Thermoelectric figure of merit ($ZT$) as a function of temperature for another sample. Here the value of $ZT$ is slight higher than the previous one.
C. Strong suppression of thermal conductivity with field

Here, \( \Delta(\sigma/\kappa) \) is defined as \( \{\sigma(B)/\kappa(B)-\sigma(0)/\kappa(0)\}/(\sigma(0)/\kappa(0)) \times 100\% \). A large enhancement (approximately 50\%) at 7 T magnetic field is mainly due to the strong suppression of electronic part of thermal conductivity, resulting a huge enhancement in thermoelectric figure of merit (ZT).

FIG. 7. (Color online) Electrical conductivity (\( \sigma \)) to thermal conductivity (\( \kappa \)) ratio under application of magnetic field.