Science Bulletin xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Science Bulletin

journal homepage: www.elsevier.com/locate/scib

Article

Magnetic-field enhanced high-thermoelectric performance in topological Dirac semimetal Cd_3As_2 crystal

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ARTICLE INFO

Article history:
Received 21 February 2018
Received in revised form 13 March 2018
Accepted 14 March 2018
Available online xxxx

Keywords:
Dirac semimetal
Thermoelectric material
Magnetic field
Enhancement of figure of merit

ABSTRACT

Thermoelectric materials can be used to convert heat to electric power through the Seebeck effect. We study magneto-thermoelectric figure of merit (*ZT*) in three-dimensional Dirac semimetal Cd_3As_2 crystal. It is found that enhancement of power factor and reduction of thermal conductivity can be realized at the same time through magnetic field although magnetoresistivity is greatly increased. *ZT* can be highly enhanced from 0.17 to 1.1 by more than six times around 350 K under a perpendicular magnetic field of 7 T. The huge enhancement of *ZT* by magnetic field arises from the linear Dirac band with large Fermi velocity and the large electric thermal conductivity in Cd_3As_2. Our work paves a new way to greatly enhance the thermoelectric performance in the quantum topological materials.

1. Introduction

Thermoelectric (TE) materials play a significant role in the energy conversion. The efficiency of such conversion depends on a dimensionless figure of merit ($ZT = (S^2/\rho)(T/\kappa)$), where S is the Seebeck coefficient, ρ is the electrical resistivity, T is the absolute temperature and κ is the thermal conductivity. The research on the TE materials for seeking high *ZT* started decades ago. How to improve the conversion efficiency is a hot topic due to the increase of energy demand and environment-friend energy. For a good TE material, high Seebeck coefficient S, low electrical resistivity ρ, and low thermal conductivity κ are required to be satisfied at the same time. However, S, ρ and κ^e (electronic contribution to κ) are usually highly coupled, so that *ZT* can be only tuned within some limitations. Though there is no theoretical limit for the value of *ZT*, the maximum *ZT* of ~1 at room temperature is observed in Bi_2Te_3, and is far from the extensive utilization of thermoelectric technology [1]. Usually, there are two routes to be used to enhance *ZT* with increasing the power factor S^2/ρ or decreasing the lattice thermal conductivity by so-called phonon engineering. To substantially reduce the lattice thermal conductivity, the phonon engineering extensively increases the phonon scattering through defect engineering [2–4], nanostructuring [5,6] (such as thin film [7,8], superlattice [9,10] and quantum dots [11]), or making the crystal structure complicated [1]. The another approach, enhancing power factor, has been realized by band engineering [2,12,13], inducing resonant level [14], ionized impurity scattering [15], modulation doping [16], and increasing carrier mobility [3,4]. Very recently, Zhao et al. [17] reported that magnetic-nanoparticles embedded in the thermoelectric matrix can tune the independent phonon- and electron-transport properties at the same time to efficiently enhance *ZT*.

It is well known that some of the good thermoelectric materials are also typical topological materials: Bi_2Te_3 and Sb_2Te_3 with topological surface states at which the conduction and valence bands touch each other at the Dirac-Cone with linear energy dispersion in all momentum directions, and the carriers have high mobility and small effective mass [18–22]. As an analogue, the 3D topological Dirac semimetal Cd_3As_2 shares similar electronic structure. The topological Dirac semimetal of Cd_3As_2 is fourfold degenerate three dimensional (3D) Dirac materials in which electrons of the bulk state have high mobility and obey linear energy dispersion, while the surface state is topology protected Fermi arc [23–25]. It has been reported that the magnetic field has a strong effect on the electric and thermal transport in topological Dirac and Weyl semimetals [26,27]. Small perturbations like strain, magnetic field

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https://doi.org/10.1016/j.scib.2018.03.010
2095-9273/

and chemical potential may tune the 3D bulk Dirac states therein [28–30], even pressure or point-contact-induced superconductivity. A non-saturation large linear magnetoresistance is observed in Cd_3As_2 [31,32], such behavior is a common feature in the topological materials with the linear energy dispersion in all momentum directions [31–35]. Cd_3As_2 is expected to be great potential for high thermoelectric performance because the ultrahigh electron mobility ($\mu \sim 10^4$–10^6 cm^2 V^{-1} s^{-1}) [31] may lead to the possible large power factor $S^2/\rho \approx \mu(m^*/m_e)$, where m^* and m_e is the energy-band electron effective mass and the free electron mass, respectively [12]. However, the experimentally achieved maximum ZT for Cd_3As_2 is only about 0.15 [36]. An anomalous thermal conductivity had been reported in Cd_3As_2 five decades ago [37]. The contribution from lattice to the thermal conductivity is quite small in Cd_3As_2 due to anion vacancy, and even much less than the contribution from electron to the thermal conductivity at room temperature [37]. Therefore, this provides possibility to dramatically enhance ZT by magnetic field to suppress the electric thermal conductivity in Cd_3As_2. It is quite different from the usual way to reduce the lattice thermal conductivity by the phonon engineering. In this work, we report magneto-thermoelectric figure of merit in 3D topological Dirac semimetal Cd_3As_2 crystal. We systematically measured temperature dependence of resistivity, thermopower and thermal conductivity under the perpendicular magnetic field in Cd_3As_2 crystal. To study the anisotropy of ZT, the crystals with [100] and [112] orientation from the same batch were used for the measurements under magnetic fields applied along [100] or [112] direction and perpendicular to electric or heat current, respectively. It is unexpected that the ZT is remarkably enhanced by a perpendicular magnetic field.

2. Experimental

The Cd_3As_2 single crystals were grown by vapor transport method, as described in our previous report [38]. Polycrystalline Cd_3As_2 was in prior synthesized by heating the stoichiometric mixtures of Cd and As powder in vacuum at 800 °C for 6 h. The Cd_3As_2 powder was loaded into a quartz tube for the growth of single crystals. The quartz tube was then evacuated, sealed and placed into a two-zone horizontal furnace. To optimize the nuclei formation, the temperature of the "cold" end (empty) and the "hot" end (containing Cd_3As_2 powders) of the tube were first raised to 520 and 575 °C, respectively, held for 6 h, then cooled to 510 and 560 °C in half an hour, respectively, and then kept there for 7–10 days. The sample with the largest dimensions of 7 mm × 2 mm × 2 mm can be achieved.

Single crystal platelets were characterized by using X-ray diffraction (XRD), performed on a SmartLab-9 diffractometer (*Rikagu Inc.*) from 10° to 70° with a scanning rate of 4° per minute. The achieved large crystals were usually oriented naturally along [100] or [112] directions (see Fig. S1 in Supplementary data). Crystals with both of [100] and [112] orientations were selected for thermoelectric measurements. Crystals were carefully polished to regular rectangular shape by keeping the flat large surface with [100] or [112] orientations unchanged before the transport measurements. The transport measurements including resistivity, thermopower and thermal conductivity were carried out by using PPMS-14 T system (*Quantum Design*). Longitudinal and Hall resistivity were measured by standard six-probe method. During the measurements, magnetic field is always applied along the crystal with [100] or [112] orientations, and electric or heat currents (I and ∇T) are perpendicular to the crystal orientation direction. Longitudinal resistivity in magnetic fields were measured by using the two same-side probes and then symmetrized between the positive and negative fields ($\rho(B) = [\rho(+B) + \rho(-B)]/2$) to cancel the picked-up Hall signal. Hall resistivity (ρ_{xy}) was measured by using the two opposite-side probes calculated through the form of $\rho_{xy}(H) = [\rho(+B) - \rho(-B)]/2$. Resistivity, thermopower and thermal conductivity in high temperatures range from 350 to 500 K and under magnetic field up to 9 T were measured by a home-built system in a bottom-loading superconducting magnet system (*American Magnetic Inc.*) with a water-cooling-protected Ta-resistance furnace inserted to provide high temperature. High-temperature thermopower and thermal conductivity were collected by adopting the longitudinal steady-state thermal flow method in high vacuum ($\sim 1 \times 10^{-4}$ Pa), with E-type chromel-constantan thermocouples of 10 μm diameter from Omega measuring the temperature differential and phosphor-bronze wires of 10 μm diameter as electric connection to measure thermopower. It has been reported that magnetic field can induce only negligible error in the measurement of temperature difference for determining the absolute values of thermal conductivity in such temperature range by using E-type thermocouples [39], so no additional calibration under magnetic field was performed. Samples were mounted on a copper heat-sink with [100] or [112] axis parallel to the magnetic field but perpendicular to I or ∇T. Heat flow for establishing the temperature gradient was supplied by a resistor chip (R = 1,820 Ω) heater, which is mounted on the hot side of the sample and thermally insulated from the copper heat-sink by a 25 cm long and 18 μm-diameter constantan wires. Small temperature gradient (~1 K) was used for thermal measurements to minimize the proportion of heat loss relative to total heat flow supplied by the heater. The radiation loss was estimated as $P_{rad} = \sigma_T \times (A_{heater} + A_{sample}/2) \times (T_{hot}^4 - T_{cold}^4)$, where $\sigma_T = 5.67 \times 10^{-8}$ W m^{-2} K^{-4} is the Stefan-Boltzmann constant, A_{heater} and A_{sample} are the surface area of the resistor chip heater and the surface area of the sample, and T_{hot} (T_{cold}) is the temperature of hot (cold) side of the sample. The actual heat flowing through the sample was then estimated by subtracting the radiation loss from the total heat flow supplied by the heater.

3. Results and discussion

Fig. 1 shows temperature dependence of resistivity in the temperature range from 2 to 500 K under magnetic fields (B) up to 14 T applied along [100] or [112] direction and perpendicular to electric current, respectively. The residual resistivity is estimated by fitting the data below 50 K with the formula of $\rho(T) = \rho_0 + AT^2$ to be ρ_0 = 0.489 and 0.587 μΩ m for the crystals with [100] and [112] orientation, respectively. The residual resistance ratios (RRR = ρ(300 K)/ρ_0) are 6.0 and 5.6 for the crystals with [100] and [112] orientation, respectively. As shown in Fig. 1, large positive magnetoresistivity is observed for the magnetic field applied along [100] or [112] direction, and resistivity monotonically increases with increasing magnetic field, being consistent with the isothermal magnetoresistivity data at 300 K as shown in Fig. S2 of Supplementary data. The magnetoresistivity (MR = [$\rho(B) - \rho(0\,T)$]/$\rho(0\,T)$) is as high as 2,600% at 3 K and 680% at 300 K for the magnetic field applied along [100] direction, and 2,400% at 3 K and 260% at 300 K for the magnetic field applied along [112] direction. It indicates that the MR for the magnetic field applied along [112] direction is much less than that for magnetic field applied along [100] direction at room temperature although their MR is nearly the same at low temperature. As shown in Fig. 1a, the crystal always shows metallic behavior in the whole temperature range for the case of the magnetic field applied along [100] direction. However, the crystal shows the metallic behavior only under magnetic field less than 4.5 T, and $\rho(T)$ changes the slope from positive to negative at certain temperature with decreasing temperature above 4.5 T for the case of the magnetic

Please cite this article in press as: Wang H et al. Magnetic-field enhanced high-thermoelectric performance in topological Dirac semimetal Cd_3As_2 crystal. Sci Bull (2018), https://doi.org/10.1016/j.scib.2018.03.010