Pressure-induced superconductivity in the three-dimensional Dirac semimetal Cd$_3$As$_2$

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The resistance of three-dimensional Dirac semimetal Cd$_3$As$_2$ was measured under pressure up to 50.9 GPa. Below 6.4 GPa, the resistance increases with applying pressure and its temperature dependence changes from metallic to insulating behavior. However, upon further increasing pressure, the resistance at low temperature decreases with pressure and superconductivity with $T_c$ ≈ 2.0 K emerges at 8.5 GPa. The $T_c$ keeps increasing to about 4.0 K at 21.3 GPa, then shows an anomalous nearly constant pressure dependence up to the highest pressure 50.9 GPa. Our observation of superconductivity in pressurized three-dimensional Dirac semimetal Cd$_3$As$_2$ provides an interesting candidate for topological superconductor.

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In recent few years, the search for topological superconductors (TSCs) has been a hot topic in condensed matter physics [1, 2]. The TSCs have a full pairing gap in the bulk and gapless surface states consisting of Majorana fermions [1]. This is in close analogy to the topological insulators (TIs), which have a full insulating gap in the bulk and gapless edge or surface states [1]. The TSC is of great importance, since it is not only a new kind of exotic superconductor, but also one source of Majorana fermions for future applications in quantum computations [1, 2].

Experimentally, the simplest way to get a candidate for TSC is to convert a TI into superconductor, by tuning the parameters such as doping or pressure. For example, by doping, Cu$_x$Bi$_2$Se$_3$ and Cu$_x$(PbSe)$_2$(Bi$_2$Se$_3$)$_6$ are considered to be candidates for TSCs [3, 5], while Sn$_{1−x}$In$_x$Te is considered as a candidate for topological crystalline superconductor [7, 8]. Under pressure, Bi$_2$Te$_3$, Bi$_2$Se$_3$, Sb$_2$Te$_3$, and Sb$_2$Se$_3$ become superconducting, which are also regarded as candidates for TSCs [9, 14]. Note that there are debates on whether these candidates are indeed TSCs [15, 17], therefore further experimental works are needed to definitely identify a TSC and manipulate the Majorana fermions on its surface.

More recently, a new kind of topological material, the three-dimensional (3D) Dirac semimetal was discovered, with examples of Na$_3$Bi and Cd$_3$As$_2$ [18, 27]. As a 3D analogue to graphene, the Fermi surface of the 3D Dirac semimetal only consists of 3D Dirac points with linear energy dispersion in any momentum direction [18, 22]. The exotic Fermi surface of Na$_3$Bi and Cd$_3$As$_2$ was confirmed by the angle-resolved photoemission spectroscopy (ARPES) experiments [19, 21, 23, 24]. The compound Cd$_3$As$_2$ is of particular interests, since it is stable in air, unlike Na$_3$Bi. Based on quantum transport measurement, a nontrivial π Berry’s phase is obtained, which provides bulk evidence for the existence of 3D Dirac semimetal phase in Cd$_3$As$_2$ [27]. By symmetry breaking, this 3D Dirac semimetal can be driven to a topological insulator or Weyl semimetal [22]. More interestingly, it is predicted that the topological superconductivity may be achieved by carrier doping [23], but this has not been realized so far. Since pressure is an effective way to induce superconductivity in TIs [9–14], it will be important to check whether superconductivity can be achieved by applying pressure on Cd$_3$As$_2$.

In this Letter, we present the resistance measurements on Cd$_3$As$_2$ single crystals under pressure up to 50.9 GPa. After an initial increase with pressure, the low-temperature resistance starts to decreases with pressure above 6.4 GPa. Superconductivity appears at 8.5 GPa with $T_c$ ≈ 2.0 K, and the $T_c$ increases to about 4.0 K at 21.3 GPa, then persists to the highest pressure 50.9 GPa. Such superconductivity observed in pressurized 3D Dirac semimetal Cd$_3$As$_2$ suggests that it may be a topological superconductor.

High-quality Cd$_3$As$_2$ single crystals were grown from Cd flux [27]. The largest natural surface was determined as (112) plane by X-ray diffraction. The resistivity in vacuum (0 GPa) was measured on a large sample with dimension of 1.50 × 0.40 mm$^2$ in the (112) plane and 0.15 mm in thickness. The resistance measurement under pressure between 1.1 and 50.9 GPa was performed using diamond anvil cell (DAC) with solid transmitting medium hexagonal boron nitride (h-BN) [9, 13, 14]. The sample size is about 80 μm × 80 μm in the (112) plane, with the thickness of ~10 μm. The pressure was determined by ruby fluorescence method at room temperature before and after each cooling down. The Cd$_3$As$_2$ single crystals measured in vacuum and under pressures are...
from the same batch.

Figure 1(a) shows the crystal structure of Cd$_3$As$_2$. The cubic Cd lattice with two vacancies resides in a face-centered cubic As lattice. Figure 1(b) plots a typical resistivity curve of Cd$_3$As$_2$ single crystal at 0 GPa.

In Fig. 2, the resistance curves for Cd$_3$As$_2$ single crystal under various pressures are plotted. From Fig. 2(a), the temperature dependence of resistance already changes to insulating behavior ($dR/dT < 0$) at 1.1 GPa. With increasing pressure, it becomes more and more insulating until 6.4 GPa. However, upon further increasing pressure, the resistance at low temperature decreases with pressure. In Fig. 2(b), it becomes more and more metallic up to 32.7 GPa. Figure 2(c) and 2(d) show the low-temperature part of the resistance curves above 8.5 GPa. A drop of resistance is observed below 2.0 K at 8.5 GPa, which should be a superconducting transition. At 11.7 GPa, the resistance drops to zero, and the transition temperature $T_c = 3.3$ K is defined at the cross of the two straight lines. The $T_c$ increases to about 4.0 K at 21.3 GPa, then persists to the highest pressure 50.9 GPa.

To make sure the resistance drop in Fig. 2 is a superconducting transition, we measure the low-temperature resistance in magnetic fields applied perpendicular to the (112) plane. Figure 3(a) and 3(b) show the low-temperature resistance at 11.7 and 13.5 GPa in various fields, respectively. At both pressures, the superconducting transition is gradually suppressed with increasing field, which demonstrates that the resistance drop is indeed a superconducting transition.

To estimate the upper critical field $H_{c2}(0)$, the temperature dependence of $H_{c2}$ is plotted in Fig. 3(c) for both 11.7 and 13.5 GPa. Although limited by the temperature range we measured, one can see an apparent linear temperature dependence of $H_{c2}$. With a linear fit to the data, $H_{c2}(0) \approx 4.29$ T is roughly estimated for 13.5 GPa. This value is much lower than the Pauli limiting field $H_{c2}^{P}(0) = 7.89$ T [30, 31], suggesting an absence of Pauli pair breaking. The linear temperature dependence of $H_{c2}$ in Fig. 3(c) is actually very interesting. It may
come from a two-band Fermi surface topology as in MgB$_2$ \cite{33,34}, or an unconventional superconducting state as in heavy-fermion compound UBe$_{13}$ \cite{35}. Similar linear temperature dependence of $H_{c2}$ has recently been observed in pressurized TSC candidates Cu$_2$Bi$_2$Se$_3$ and Bi$_2$Se$_3$, and in non-centrosymmetric superconductor YPtBi under ambient and high pressures, which was considered as an indication of unconventional superconducting state \cite{11} \cite{36} \cite{37}.

We notice that no superconductivity was observed up to 13.43 GPa in an earlier pressure study of Cd$_3$As$_2$ single crystal \cite{38}. The possible reason is that their sample is slightly different from ours and pressure higher than 13.43 GPa is needed to induce superconductivity. Interestingly, we also notice two recent point contact studies on Cd$_3$As$_2$ polycrystal and single crystal, respectively \cite{39} \cite{40}. In both studies, indication of superconductivity was found around the point contact region on the surface \cite{39} \cite{40}. In particular, no superconductivity is observed by the “soft” point contact technique, therefore it was suggested that the superconductivity observed around the point contact region under the “hard” tip might be induced by the local pressure \cite{40}. While these point contact studies are consistent with our result, the superconductivity observed by our bulk resistance measurement under hydrostatic pressure is more convincing.

In Fig. 4, we plot the pressure dependence of $T_c$ for Cd$_3$As$_2$. There is apparently a region of constant $T_c$ from 21.3 to 50.9 GPa. Such a phase diagram is very similar to that of 3D TI Bi$_2$Se$_3$, which also shows a nearly constant $T_c$ from 30 to 50 GPa after an initial increase of $T_c$ starting from 12 GPa \cite{11}. A constant $T_c$ over such a large pressure range is highly anomalous, as Kirshenbaum et al. already pointed out \cite{11}. For Bi$_2$Se$_3$, two mechanisms with contrasting pressure-dependant $T_c$ may be balanced so as to produce a pressure-invariant $T_c$ over a wide range of pressure \cite{11}. It was argued that the unique pressure evolution of $T_c$ and the anomalous linear temperature dependence of $H_{c2}$ are two evidences for a very unconventional superconductivity in Bi$_2$Se$_3$ \cite{11}. Due to the similarities, this may be also the case for Cd$_3$As$_2$.

To discuss whether this superconducting state of Cd$_3$As$_2$ under pressure is topological, it is necessary to know the band structure of Cd$_3$As$_2$ under pressure. Since the band structure relies on the crystal structure, it is important to know whether the crystal structure changes with applying pressure. Indeed, for the 3D TI Bi$_2$Se$_3$, there is a transition from $R\text{-}3\text{m}$ to a sevenfold ($C/2\text{m}$) structure near 10 GPa, followed by another one to a bcc-like ($C/2\text{m}$) structure above 28 GPa \cite{11}. In the the earlier pressure study of Cd$_3$As$_2$, it was found that Cd$_3$As$_2$
undergoes a structural phase transition at 2.57 GPa [38]. For our Cd$_3$As$_2$ sample, our preliminary Raman spectra measurements show additional vibration mode above 10 GPa, indicating possible structure change. This may relate to the emergence of superconductivity we observe. More detailed crystal structure measurement and band structure calculation under pressures are currently ongoing.

In summary, we have done resistance measurements on the 3D Dirac semimetal Cd$_3$As$_2$ single crystals under pressures up to 50.9 GPa. Below 6.4 GPa, the resistance behavior becomes more and more insulating with increasing pressure, however it changes back to metallic again at higher pressures. Superconductivity emerges at 8.5 GPa. The $T_c$ increases from 2.0 K at 8.5 GPa to 4.0 K at 21.3 GPa, then it shows an anomalous constant pressure dependence up to the highest pressure measured. Our observation of superconductivity in Cd$_3$As$_2$ provides another interesting candidate for topological superconductor, although further works are needed to verify it.

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