Emergence of Superconductivity on the Border of Antiferromagnetic Order in RbMn$_6$Bi$_5$ under High Pressure: A New Family of Mn-Based Superconductors

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(Received 28 March 2022; accepted 21 April 2022; published online 5 May 2022)

We report the discovery of superconductivity on the border of antiferromagnetic order in a quasi-one-dimensional material RbMn$_6$Bi$_5$ via measurements of resistivity and magnetic susceptibility under high pressures. Its phase diagram of temperature versus pressure resembles those of many magnetism-mediated superconducting systems. With increasing pressure, its antiferromagnetic ordering transition with $T_N = 83$ K at ambient pressure is first enhanced moderately and then suppressed completely at a critical pressure of $P_c \approx 13$ GPa, around which bulk superconductivity emerges and exhibits a dome-like $T_c(P)$ with a maximal $T_c^{\text{onset}} \approx 9.5$ K at about 15 GPa. In addition, the superconducting state around $P_c$ is characterized by a large upper critical field $\mu_0 H_c(0)$ exceeding the Pauli paramagnetic limit, implying a possible unconventional pairing mechanism. The present study, together with our recent work on KMn$_6$Bi$_5$ (the maximum $T_c^{\text{onset}} \approx 9.3$ K), makes AMn$_6$Bi$_5$ ($A = \text{alkali metal}$) a new family of Mn-based superconductors with relatively high $T_c$.

DOI: 10.1088/0256-307X/39/6/067401

The advances in the field of unconventional superconductivity are largely driven by the discovery of novel superconducting systems, especially those derived from the parent compounds with antiferromagnetic (AFM) order, as exemplified by the cuprates and iron-pnictide high-temperature superconductors.\cite{1-3} The first-row ($3d$) transition-metal-based compounds are at the forefront of materials’ discovery for unconventional superconductivity due to the presence of strong electronic correlations and the proximity to magnetic instability. In 2015, we discovered pressure-induced superconductivity in MnP with the critical temperature ($T_c$) about 1 K by suppressing its helimagnetic order under high pressure.\cite{4} This finding breaks the general wisdom about Mn’s antagonistic to superconductivity and has thus promoted the quest for more Mn-based superconductors with higher $T_c$. After years of explorations, we recently found that KMn$_6$Bi$_5$ with a unique quasi-one-dimensional (Q1D) structure becomes superconducting with a relatively high $T_c^{\text{onset}}$ up to 9.3 K when its antiferromagnetic order is suppressed by pressure.\cite{5} This finding makes KMn$_6$Bi$_5$ the first ternary Mn-based superconductor with an optimal $T_c$ about an order higher than that of MnP. Importantly, this result demonstrates that the $T_c$ of Mn-based superconductors has a potential to go higher. In addition, the obtained temperature-pressure phase diagram of KMn$_6$Bi$_5$, featured by a superconducting dome on the border of antiferromagnetic order, resembles those of many unconventional superconducting systems associated with magnetism-mediated pairing mechanism.\cite{6-8} Since KMn$_6$Bi$_5$ is one member of the Q1D AMn$_6$Bi$_5$ ($A = \text{alkali metal}$) system,\cite{9-11} it is natural to ask whether they consist of a new family of Mn-based superconductors. To address this issue, here we turn our attention to RbMn$_6$Bi$_5$.

As shown in Fig. 1(a), RbMn$_6$Bi$_5$ also adopts the monoclinic structure (space group $C2/m$) featured by the infinite [Mn$_6$Bi$_5$$^-$] columns, which are composed of an outer nanotube of Bi atoms, an inner Mn–Mn bonded metallic pentagon core and a one-dimensional Mn–Mn atomic chain in the center along the $b$ axis. The counter-cation Rb$^+$ ions fill the space between the [Mn$_6$Bi$_5$]$^-$ columns, acting as the structural frame and carriers’ source.\cite{9-11} Replacing K$^+$ with a larger radius ion Rb$^+$ in AMn$_6$Bi$_5$ leads to anisotropic expansions of lattice parameters, i.e., the...
Through detailed measurements of resistivity and magnetic susceptibility at high pressures, here we show that RbMn$_6$Bi$_5$ becomes superconducting when its antiferromagnetic order is suppressed by pressure at a critical pressure of $P_c \approx 13$ GPa. The maximal $T_c$ onset $\approx 9.5$ K is achieved at $\approx 15$ GPa. In addition, the superconducting state around $P_c$ is characterized by a large upper critical field $\mu_0 H_c2(0)$ exceeding the Pauli limit, indicating a possible unconventional pairing mechanism. Along with our recent work on KMn$_6$Bi$_5$,[5] the present study establish AMn$_6$Bi$_5$ as a new family of ternary Mn-based superconductors with relatively high $T_c$, which should be subjected to further experimental and theoretical investigations.

**Experimental.** RbMn$_6$Bi$_5$ single crystals were grown by using the Rb-Bi flux method as reported previously.[10] We measured single-crystal x-ray diffraction (XRD) at 300 K and confirmed that RbMn$_6$Bi$_5$ crystallizes in a monoclinic structure with space group C2/m. The refined lattice parameters are consistent with the previous report.[10] Energy dispersive spectroscopy (EDS) measurements on the fresh surface of crystals confirm that the average chemical composition, Rb:Mn:Bi = 1:6.11:5.08, is close to the stoichiometric ratio. Electrical transport and magnetic properties at AP were measured with the Quantum Design Physical Property Measurement System (PPMS) and Magnetic Property Measurement System (MPMS-III), respectively.

High-pressure transport and ac magnetic susceptibility were performed in the palm-type cubic anvil cell (CAC) apparatus with high hydrostatic pressures.[16,17] Standard four-probe method was employed for resistivity measurement with the current applied along the $b$-axis. As shown in the inset of Fig. 2, the sample is tilted in the Teflon cell of CAC in order to prevent it from rotating so as to protect the electrical contacts during compression. Thus, the angle between magnetic field and the $b$-axis is about 45$. The sample-1 size in CAC is about 0.10 × 0.12 × 0.55 mm$^3$. AC magnetic susceptibility was measured by mutual induction method at a fixed frequency and the sample-2 size is about 0.30 × 0.30 × 0.25 mm$^3$. The primary and secondary coils are made of enameled copper wires of 25 $\mu$m in diameter. Glycerol was employed as the pressure transmitting medium. The pressure values inside the CAC were determined from the superconducting transition of Pb at low temper-

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**Fig. 1.** (a) Crystal structure of RbMn$_6$Bi$_5$. (b) Temperature dependence of the resistivity and magnetic susceptibility along the rod direction of RbMn$_6$Bi$_5$ crystal at AP. The $T_N$ shows the antiferromagnetic transition temperature.

The Curie–Weiss fitting is shown by the broken line. Inset of (b) shows a picture of the RbMn$_6$Bi$_5$ crystal.
Results. The RbMn$_6$Bi$_5$ crystals are black in color with metallic luster and have a needle shape with the longest dimension along the $b$-axis. They were first characterized at AP via measurements of electrical resistivity $\rho(T)$ and magnetic susceptibility $\chi(T)$ along the rod direction. As shown in Fig. 1(b), the $\rho(T)$ of RbMn$_6$Bi$_5$ shows a metallic behavior in the whole temperature range and exhibits a clear hump anomaly around 83 K, where a sudden drop in $\chi(T)$ appears. The estimated residual resistivity ratio [RRR $\equiv \rho(300 \text{ K})/\rho(2 \text{ K})$] for the RbMn$_6$Bi$_5$ crystal is about 17, and the Curie–Weiss fitting to the paramagnetic susceptibility above 100 K yields an effective moment of 1.68$\mu_B$/Mn. These values are close to those reported in literature.\cite{10} It should be noted that the observed $\rho(T)$ is different from that reported in Ref.\cite{10} along the $b$-axis. Here, the observed upturn feature indicates the inclusion of contribution from $\rho_L$. As shown in the inset of Fig. 1(b), the RbMn$_6$Bi$_5$ crystals are soft and are composed of a bundle of thin fibers, consistent with the Q1D character of the crystal structure. Such a character makes it easy to pick up the signal perpendicular to the $b$-axis when measuring resistivity of the bulk crystal with the standard four-probe configuration. Nonetheless, these measurements confirm the metallic nature of RbMn$_6$Bi$_5$ with an antiferromagnetic ordering transition at $T_N = 83$ K.

Figure 2(a) shows the resistance $R(T)$ data of RbMn$_6$Bi$_5$ crystal (sample 1) measured along the $b$-axis under various hydrostatic pressures up to 14.5 GPa in a CAC apparatus. The overall evolutions of $R(T)$ under high pressure are similar to those observed in KMn$_6$Bi$_5$.\cite{5} At 2 GPa, the $R(T)$ shows a saturation behavior at high temperatures and a weak inflection point around $T_N$, followed by a broad hump at low temperatures. Here, $T_N$ can be determined from the peak of $dR/dT$, Fig. 2(d). With increasing pressure, the resistance is reduced progressively and the features around $T_N$ and below are weakened gradually; the $T_N$ values determined from local maximum of $dR/dT$ are enhanced slightly from 83 K at AP to ~93 K at 6 GPa, Figs. 2(e)–2(f). Upon increasing pressure to 8 GPa, the $R(T)$ behaves differently, and the downward inflection feature around $T_N$ evolves into a weak hump-like anomaly; the corresponding anomaly in $dR/dT$ changes to a broad dip, Fig. 2(g). Similar crossover is also found in the resistance of KMn$_6$Bi$_5$ and may be associated with the...
modification of the antiferromagnetic structure under pressure and/or the emergence of spin density wave above 8 GPa in RbMn$_5$Bi$_3$. With further increasing pressure, the hump anomaly is weakened and $T_N$ is reduced gradually, reaching $\sim$46 K at 12 GPa [Fig. 2(i)]. No clear anomaly can be discerned in the $R(T)$ of 12.5 GPa [Fig. 2(j)], indicating that the long-range antiferromagnetic order in RbMn$_5$Bi$_3$ has been suppressed completely.

Accompanying the collapse of antiferromagnetic order in RbMn$_5$Bi$_3$, we observed a sudden drop of resistance at low temperatures, signaling the possible occurrence of superconductivity. Here we define the onset and zero-resistivity temperatures of the superconducting transition, $T^{\text{onset}}$ and $T^{\text{zero}}$, as the temperatures where the resistance starts to deviate from high-temperature linear extrapolation and reduces to nearly zero, respectively. As shown in Fig. 2(b), the $R(T)$ at 13 GPa starts to decrease at $T_d^{\text{onset}} \approx 6.6$ K, and zero resistance can be reached below $T_d^{\text{zero}} \approx 2.3$ K at 13.5 GPa. With increasing pressure, the superconducting transition moves to higher temperatures gradually; $T^{\text{onset}}$ and $T^{\text{zero}}$ at 14.5 GPa reach about 9.2 K and 4.3 K, respectively. The observed optimal $T_d$ value of RbMn$_5$Bi$_3$ is close to that of KMn$_5$Bi$_3$ ($\sim$9.3 K), and is much higher than that of MnP ($\sim$1 K).

To characterize the superconducting state, $R(T)$ under different magnetic fields were recorded at 13.5, 14, and 14.5 GPa for RbMn$_5$Bi$_3$. As shown in Figs. 3(a)–3(c), with increasing magnetic field the superconducting transition is shifted to lower temperatures and broadened up gradually owing to the magnetic-breaking effect and the flux creep effect in the vortex state. Here, we employed the criteria of 50% $R_n$ to determine $T_d$ at each field and plotted the temperature dependence of $\mu_0 H_c^2(T)$ in...
Fig. 3(d). The zero-temperature upper critical field \( \mu_0 H_{c2}(0) \) is obtained by fitting the experimental data to the Ginzburg–Landau (G-L) equation, \( \mu_0 H_{c2}(T) = \mu_0 H_{c2}(0)[1 - (T/T_c)^2]/[1 + (T/T_c)^2] \).\(^{[18]}\) Then, the coherence length \( \xi(0) \) can be calculated according to the relationship: \( \mu_0 H_{c2}(0) = \Phi_0/2\pi \xi(0)^2 \), where \( \Phi_0 = h/2e = 2.067 \times 10^{-15} \) Wb is the magnetic flux quantum. As seen in Fig. 3(d), \( \mu_0 H_{c2}(0) \) increases dramatically from 9.7 T at 13.5 GPa to 18.0 T at 14.5 GPa, the latter value being well above the Pauli limit of \( \mu_0 H_p = 1.84 T_c = 11.1 \) T.\(^{[19]}\) Accordingly, the value of \( \xi(0) \) decreases from 58.2 Å at 13.5 GPa to 47.5 Å at 14.5 GPa. The presences of large \( \mu_0 H_{c2}(0) \) and small coherence length are the common features of unconventional superconductivity.\(^{[19,20]}\)

We note that the \( \mu_0 H_{c2}(T) \) curve displays a tail near 0 T, which cannot be well described by the simple G-L fitting, suggesting the presence of multi-band effect.\(^{[21,22]}\) We thus also fit the data by adopting two-band model as shown in Fig. 3(d) and the estimated \( \mu_0 H_{c2}(0) \) are about 9.85 T, 13.05 T and 15.66 T for 13.5 GPa, 14 GPa and 14.5 GPa, respectively. Although the obtained \( \mu_0 H_{c2}(0) \) values with the two-band model are smaller than that obtained with G-L fitting, they still exceed the Pauli limit. In addition to the unconventional pairing mechanism, other effects such as the multi-band behavior, strong electronic correlations and strong coupling may also contribute to the observed large \( \mu_0 H_{c2}(0) \) in RbMn\(_5\)B\(_5\), which requires more studies in the future.

Figure 3(e) shows the ac magnetic susceptibility \( \chi'(T) \) for RbMn\(_5\)B\(_5\) crystal (sample 2) and a piece of Pb, which serves as a superconducting reference to estimate the superconducting shielding volume fraction of RbMn\(_5\)B\(_5\). The pressure values in Fig. 3(e) were estimated based on the superconducting \( T_c \) of Pb. As can be seen, only the superconducting transition of Pb is observed at \( P \leq 12.3 \) GPa, and the sharp transitions elaborate an excellent hydrostatic pressure environment in CAC. At \( P \geq 13.6 \) GPa, in addition to the sudden drop of \( \chi'(T) \) for Pb, we observed a gradual reduction of \( \chi'(T) \) below the superconducting critical temperature \( T_c^\text{DAC} \) of RbMn\(_5\)B\(_5\). In accordance with the resistance data shown in Fig. 2(b), \( T_c^\text{DAC} \) also increases with pressure and reaches about 8 K at 14.5 GPa. The superconducting shielding volume fraction also increases with decreasing temperature, and reaches nearly 100% at 1.5 K, confirming the bulk nature of the observed superconductivity in RbMn\(_5\)B\(_5\).

To track the evolution of the superconducting transition at higher pressures, we measured the \( R(T) \) of RbMn\(_5\)B\(_5\) crystal (sample 3) by using a diamond anvil cell (DAC) up to 23.3 GPa. Except for the \( R(T) \) data at 13.8 GPa, other curves in Fig. 3(f) have been shifted down vertically for clarity. As seen in Fig. 3(f), the superconducting transition can be clearly detected as a drop of resistance below \( T_c^\text{DAC} \), but the zero resistance cannot be achieved, presumably due to the non-hydrostatic pressure conditions in DAC employing a solid pressure transmitting medium. Similarly, the \( T_c^\text{DAC} \) is defined where the resistance starts to deviate from the linear extrapolation. With increasing pressure in DAC, \( T_c^\text{DAC} \) increases monotonously from ~8.2 K at 13.8 GPa to a maximum of ~9.5 K at 15.5 GPa, and then decreases gradually to ~4.1 K at 23.3 GPa, giving rise to a superconducting dome as shown below. Concomitant with the reduction of \( T_c \), the drop of resistance below \( T_c \) also becomes smaller.

Based on the above experimental results obtained using CAC and DAC, we can construct a \( T-P \) phase diagram for RbMn\(_5\)B\(_5\) as summarized in Fig. 4. With increasing pressure, \( T_N(P) \) first increases moderately from 83 K at AP to ~93 K at 6 GPa, where it experiences a sudden drop and then decreases gradually until it vanishes abruptly at a critical pressure of \( P_c \approx 13 \) GPa. For most antiferromagnetic metals, \( T_N(P) \) decreases monotonically with pressure. In the present case, the initial increase of \( T_N \) from AP to ~6 GPa may be attributed to the enhanced intercolumn exchange interactions. The modification of relative strength of intercolumn to intracolumn interactions may alter the magnetic structure around 6 GPa, which then induces the changes of characteristic anomalies in \( \rho(T) \) and \( d\rho/dT \) around \( T_N \). Such a crossover is similar to that observed recently in the Kagome metal CsV\(_3\)Sb\(_5\) under pressure associated with an anisotropic lattice compressibility and modification of change density wave.\(^{[23]}\) Bulk superconductivity emerges at about 13 GPa and zero-resistance state is achieved at 13.5 GPa. \( T_c(P) \) increases monotonously to a maximal value of \( T_c^\text{DAC} \approx 4.1 \) K at 23.3 GPa.
9.5 K at 15.5 GPa and then decreases gradually with further increasing pressures. These features define a pressure-induced superconducting dome on the border of long-range antiferromagnetically ordered state (see Fig. 4). Such a $T–P$ phase diagram of RbMn$_6$Bi$_5$ is almost identical to that of KMn$_6$Bi$_5$ and resembles those of many unconventional superconducting systems associated with magnetism-mediated pairing mechanism.\[6\,8\,19]

Discussions. The discovery of pressure-induced superconductivity with a relatively high $T_c \approx 9$ K in the Q1D materials (K/Rb)Mn$_6$Bi$_5$ is quite encouraging and will stimulate more studies in related Mn-based superconductors.

Firstly, (K/Rb)Mn$_6$Bi$_5$ represent a new class of ternary Mn-based superconductors with unique Q1D crystal structure and possible novel [Mn$_6$Bi$_5$]$^-$ superconducting gene. As mentioned above, the Mn-based superconductors are quite rare owing to the strong magnetic pair-breaking effect. So far, pressure-induced superconductivity has been observed only in the binary MnP and MnSe.\[4\,24\] In these cases, other tuning methods expect for applying pressure are less effective in regulating the magnetism and inducing superconductivity so far. In contrast, the ternary AMn$_6$Bi$_5$ with a flexible Q1D structure provides more possibilities to tune the physical properties at AP, e.g., via carrier doping or chemical substitutions at the A- and/or Bi-sites.

Secondly, they offer a new material platform to study the interplay between exotic magnetism and superconductivity. The magnetic structure of AMn$_6$Bi$_5$ has not been resolved experimentally. According to the density-functional-theory calculations, RbMn$_6$Bi$_5$ could adopt a complex helical antiferromagnetic structure at AP.\[10\] As pointed out previously for MnP,\[4\,29\] the emergence of superconductivity in a helical magnet is rare; it deserves in-depth studies to understand the role of spin fluctuations associated with helical order in driving superconductivity. In this regard, it is highly desirable to determine the magnetic structure of AMn$_6$Bi$_5$ at AP and then to reveal its evolution under high pressures. In addition, the information about the spin dynamics near the antiferromagnetic QCP around $P_c$ are also important to understand the superconducting mechanism.

Thirdly, considering the fact that the observed large $\mu_0H_{c2}(0)$ exceeds the Pauli paramagnetic limit, it is interesting to investigate the superconducting pairing mechanism. For example, spin-triplet superconducting state has been proposed and verified by the nuclear magnetic resonance (NMR) experiments in the Q1D superconductor $A_2$Cr$_3$As$_3$, which possesses a similar crystal structure and unusually large $\mu_0H_{c2}(0)$.\[15\,26\,27\] Thus, the NMR experiments under high pressure on (K/Rb)Mn$_6$Bi$_5$ are highly desirable to investigate the superconducting gap symmetry.

Last but not least, although the Mn-based compounds are commonly believed to be antagonistic to superconductivity and thus should have a low $T_c$, the present work demonstrates that the transition temperature of Mn-based superconductors can be raised at least to the level of 10 K. Our work thus calls for more investigations on AMn$_6$Bi$_5$ and other complex Mn-based compounds with an aim to further raise the $T_c$ of Mn-based superconductors.

In summary, we report the discovery of superconductivity on the border of antiferromagnetic order in the Q1D RbMn$_6$Bi$_5$ under pressure. Bulk superconductivity emerges and display a superconducting dome with the maximal $T^{\text{ onset}}_c \approx 9.5$ K at about 15 GPa. The constructed $T–P$ phase diagram and the usually large upper critical field $\mu_0H_{c2}(0)$ exceeding the Pauli paramagnetic limit suggest an unconventional superconducting pairing mechanism for RbMn$_6$Bi$_5$. Along with our recent work on KMn$_6$Bi$_5$, the present study establishes that AMn$_6$Bi$_5$ ($A = \text{alkali metal}$) represent a new family of ternary Mn-based superconductors with relatively high $T_c$. More studies are needed to reveal the complex magnetism and its relationship with the observed superconductivity.

Acknowledgements. This work was supported by the Beijing Natural Science Foundation (Grant No. Z190008), the National Key R&D Program of China (Grant Nos. 2018YFA0305700 and 2021YFA1400200), the National Natural Science Foundation of China (Grant Nos. 12025408, 11874400, 11834016, 11921004, 11904391, 12174424, and 1188101), the Strategic Priority Research Program and Key Research Program of Frontier Sciences of CAS (Grant Nos. XDB25000000, XDB33000000 and QYZDB-SSW-SLH013), the CAS Interdisciplinary Innovation Team (Grant No. JCTD-201-01), K. C. Wong Education Foundation (GJTD-2020-01), the Users with Excellence Program of Hefei Science Center CAS (Grant No. 2021HSC-UE008), Youth Promotion Association of CAS (Grant No. 201801), and Y.U. acknowledges the support from JSPS KAKENHI (Grant No. JP19H00648).

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