Evidence for superconductivity in Rb metal above 55 GPa pressure

Yuhang Deng and James S. Schilling
Department of Physics, Washington University, St. Louis, Missouri 63130, USA

(Received 17 May 2019; published 15 July 2019)

The only alkali metal known to be superconducting at ambient pressure is Li at 0.4 mK. Under 30 GPa pressure $T_c$ for Li rises to 14 K. In addition, nearly 50 years ago the heavy alkali metal Cs was reported to become superconducting near 1.3 K at 12 GPa. In the present experiment the superconductivity of Cs under pressure is confirmed. In addition, strong evidence is presented in electrical resistivity measurements that neighboring Rb also becomes superconducting near 2 K at 55 GPa as it enters the $\alpha$C16 phase, as for Cs, where $T_c$ decreases under the application of pressure. It would seem likely that under the right temperature/pressure conditions all alkali metals, including metallic hydrogen, will join the ranks of the superconducting elements. With the addition of Rb, 55 of the 92 naturally occurring elements are superconducting at ambient or high pressure.

DOI: 10.1103/PhysRevB.100.041109

At first glance the alkali metals would appear to be rather mundane compared to the other elemental solids in the periodic table: None of the alkali metals are magnetic and only one, Li, is known to be superconducting at ambient pressure, but then only at the exceedingly low temperature of $T_c \simeq 0.4$ mK [1]. Their simple bcc structure and free-electron character make the alkali metals ideal simple metals with very nearly spherical Fermi surfaces. As for all monovalent metals, their low electronic density of states favors weak electron-phonon interactions that are insufficient, except for Li, to support superconductivity [2].

The large atomic volume and very high compressibility of all alkali metals lead to significant changes in their properties under the application of very high pressures. The atomic volume of Cs metal shrinks fivefold under $\sim$50 GPa [3]. As a result, the once free-electron alkali metals with a cubic bcc crystal structure become electrides under sufficient pressure where the conduction electrons no longer surround each cation but are forced into interstitial lattice sites [4], becoming de facto anions [5]. In addition, the marked pressure-induced changes in the character of the conduction electrons through $s$-$p$ transfer in Li and Na and $s$-$d$ transfer in K, Rb, and Cs are believed to destabilize the highly symmetric low-pressure structures (bcc, fcc) and favor complex, lower-symmetry structures [6]. Another result of the marked change in conduction electron character is that the superconducting transition temperature of Li soars from 0.4 mK at ambient pressure to 14 K at 30 GPa [7], an increase of over four orders of magnitude.

Superconductivity in Cs near 1.3 K was reported many years ago by Wittig [8] for pressures near 12 GPa, close to the pressure where Cs enters the orthorhombic $\alpha$C16 phase [9]. In the Supplemental Material [10] very recent experiments are presented that confirm these early results. It would seem likely that all alkali metals will become superconducting under pressure, yet no superconductivity has been found for the following: Na in the pressure/temperature ranges to 58 GPa above 4 K [2]; K to 17 GPa above 1.5 K or to 44 GPa above 4 K [2], as well as to 94 GPa above 1.35 K [13]; and Rb to 21 GPa above 50 mK [14]. Schwarz et al. [15] have suggested that a search for Rb should be carried out for pressures of 50 GPa and above since this is the pressure where Rb takes on the same $\alpha$C16 phase where Cs becomes superconducting.

In the present electrical resistivity studies on Rb the pressure range of previous work has been extended to $\sim$80 GPa for temperatures above 1.3 K. Strong evidence is given for the appearance of superconductivity in Rb near 2 K following a sluggish phase transition at 50 GPa from the tetragonal $t$4 to the orthorhombic $\alpha$C16 phase. Rb thus becomes the 55th elemental superconductor in the periodic table.

Polycrystalline Cs (99.98 % pure) and Rb (99.75 % pure) samples were obtained in sealed glass ampoules from Alfa Aesar. A diamond anvil cell (DAC) made of conventional and binary CuBe [16] was used to generate pressures to $\sim$80 GPa between two opposed diamond anvils (1.6 carat, type Ia) with 0.5-mm-diam culets. The force applied to the anvils was generated by a stainless-steel diaphragm filled with He gas [17]. The Re gasket (250 $\mu$m thick) was preindent to 80 $\mu$m and a 250-$\mu$m-diam hole drilled through the center of the preindentation area. A cubic boron nitride (cBN)-epoxy insulation layer was compressed onto the surface of the gasket (see Fig. 1). Four Pt strips (4 $\mu$m thick) were then placed on the insulation layer, acting as electrical leads for the four-point resistivity measurement. Further details are published elsewhere [18,19].

Whereas a small, thin lanthanide sample was normally placed on top of the four Pt strips (see Fig. 1 in Ref. [19]), the extreme softness of the alkali metals led to large sample extrusion out of the cell, necessitating shaping a bowl in the cBN-epoxy cell to contain the alkali metals, as illustrated in Fig. 1. Because of their extreme air sensitivity, the Cs and Rb samples were loaded into the bowl-shaped chamber inside a glove box filled with ultrahigh-purity Ar gas.

The DAC was inserted into an Oxford flow cryostat capable of varying temperature from ambient to 1.3 K. Pressure was determined at room temperature using the diamond vibron [20]. With a ruby manometer the pressure can normally be measured in situ over the entire temperature range [21].
FIG. 1. Schematic drawing of pressure cell with Re gasket used in the present four-point electrical resistivity experiments on pure Cs and Rb. Unlike the standard configuration (see Fig. 1 in Ref. [19]), here a bowl is formed in the central cBN/epoxy section to contain the soft alkali metals. The opposing diamond anvil presses downward from above generating pressures to $\sim80$ GPa.

Unfortunately, the ruby sphere would normally sink into the soft alkali metal, the $R1$ fluorescence being lost. However, in one experiment to 14 GPa on Cs the ruby fluorescence could be detected to low temperatures, revealing a pressure increase of $\sim17\%$ on cooling from 295 to 4 K. This pressure increase was used in experiments on both Cs and Rb to estimate the pressure at low temperatures from the measured vibron pressure at ambient temperature.

In Fig. 2 the resistance of Rb at ambient temperature (295 K) is plotted versus both increasing and decreasing pressure. Initially the pressure was slowly increased along the black line to 73 GPa, then decreased to 34 GPa, followed by an increase along the red line to 75 GPa, then decreased to 48 GPa. The many structural phase transitions that occur in pure Rb over this pressure range are shown at the top of the graph [22]. A small peak in $R(P)$ marks the bcc $\rightarrow$ fcc transition 7 GPa with a much more prominent structure in $R(P)$ for the next transitions. In the tetragonal $tI_4$ phase the resistance changes little with pressure, but begins to increase sharply after passing the $tI_4 \rightarrow oC16$ phase boundary at 48 GPa. The sizable hysteresis in $R(P)$ reveals the first-order nature of this transition that is reportedly very sluggish at ambient temperature [15]. The $R(P)$ dependence and structural phase diagrams at ambient temperature for Cs bear a marked similarity to those for Rb in Fig. 2 if the differences in the transition pressures are taken into account, as seen in the Supplemental Material [10].

In Fig. 3 the temperature-dependent resistance of Rb is displayed for 61, 75, and 48 GPa, measured in that order, as seen by comparing the order of measurement numbers to those in Fig. 2. At all three pressures a sharp drop in the resistance is observed near 2 K (see the inset in Fig. 3 for 56 GPa), as would be expected for a superconducting transition. As discussed below, it is common in superconducting alkali metals that the resistivity fails to disappear completely
in high-pressure experiments. A marked negative curvature is evident in the temperature dependence of the resistance, a hallmark of transition metals. This is clear evidence for strong d character in the conduction electrons of Rb at these very high pressures arising from s-d electron transfer.

In Fig. 4 a sharp drop in the resistance is also observed for Rb at 71 GPa. As the magnet field is increased to 480 G, the sharp drop is seen to shift to progressively lower temperatures at the rate $\sim 1$ mK/G. The sharp resistance drop plus the shift of the transition to lower temperatures in a magnetic field give strong evidence that Rb metal becomes superconducting for pressures above 56 GPa.

In the inset in Fig. 4 the dependence of the critical temperature on magnetic field is plotted at both 71 and 77 GPa. From a fit to these data using the standard expression $H_c(T) = H_0[1 - (T/T_c)^2]$ [23], the critical field at 0 K, $H_0$, can be estimated for Rb to be $H_0 \approx 1370$ and 1310 G at 71 and 77 GPa, respectively. In the Supplemental Material [10] it is pointed out that for Cs, $H_0 \approx 270$ G at 15.1 GPa. For Li from Ref. [7], $H_0 \approx 800$ and 1000 G at 22 and 24 GPa, respectively.

In Fig. 5 the dependence of the resistance of Rb on temperature is plotted to 3 K at various pressures. Except for the data at 56 GPa, the transition temperature $T_c$ is seen to decrease monotonically with increasing pressure. Interestingly, the resistance at 3 K shows a nonmonotonic pressure dependence that reflects that shown in Fig. 2 for the resistance at room temperature. The dependences of $T_c$ on pressure from Fig. 5 and a second experiment are shown in Fig. 6, yielding from the straight-line fit the value $dT_c/dP \simeq -39$ mK/GPa.

From the above results it is clear that superconductivity in Rb above 1.3 K only occurs in its oC16 phase, but not in the tI4 phase. As this sluggish phase transition begins with increasing pressure, the resistivity starts to rise, as seen in Fig. 2. At 48 GPa the sample is still in the tI4 structure and no superconductivity is observed. However, upon increasing pressure to 56 GPa (points 1 or 12) the resistance has clearly increased, indicating that at least some of the tI4 phase has transitioned to oC16. That only a partial superconducting transition is seen for points 1 and 12 (see Fig. 5 for point 12) shows that at 56 GPa the sample is still in a mixed phase region. As the pressure is increased further to 75 GPa (points 12–16 or 1–7 in Fig. 2), the resistivity begins to saturate, possibly indicating the phase transition to oC16 is nearing completion. At the same time the superconducting transition becomes more complete. At no pressure does the resistance get closer than 98% to zero. This effect of nonzero resistance observed here for Rb as well as for Cs in the Supplemental Material [10] and earlier by Ullrich [24,25], arises from the nonideal geometry in the resistivity experiment and the inhomogeneous pressure distribution across the sample. Studies of the ac susceptibility and resistivity on Rb and Cs to temperatures well below 1.3 K are recommended.

Since the superconducting transition temperature $T_c$ for Rb decreases monotonically with increasing pressure, the highest value of $T_c$ would occur at the lowest pressure, as long as the sample remains in the high-pressure oC16 phase. These facts were used to maximize the value of $T_c$ by decreasing pressure from point 16 to 17 (or from point 7 to points 10 or 11) in Fig. 2 where Rb is still mainly in the oC16 phase on unloading due to the large $\sim 15$ GPa hysteresis in $R(P)$.
Indeed, the $R(T)$ data in Fig. 5 for points 10, 11, and 17 place $T_c$ in the range 2.2–2.5 K, the highest values measured in the present experiment.

The importance of the $oC16$ phase for the appearance of superconductivity above 1.3 K is not restricted to Rb but also applies to neighboring Cs, as emphasized by Schwarz et al. [15]. Once in the $oC16$ phase, the transition temperature $T_c$ for both Rb and Cs is observed to decrease with increasing pressure. In addition, for Cs the transition between the same two phases $tI4 \rightarrow oC16$ is accompanied by a marked increase in the resistivity, as seen in the Supplemental Material [10]. In electronic structure calculations on Rb by Fabbris et al. [26], a prominent peak structure already appears in the density of states near the Fermi level for pressure near 16 GPa, the conduction electrons taking on a significant $d$ character. At the $fcc \rightarrow oC52$ phase transition a sizable enhancement in the density of states occurs. Perhaps the sudden appearance of superconductivity in Rb near 55 GPa is the result of a similar enhancement at the $tI4 \rightarrow oC16$ phase transition.

In the next lighter alkali metal K the $tI4 \rightarrow oC16$ transition also occurs, but not until the much higher pressure of 96 GPa [27]. Debessai [13] found no superconductivity in K above 1.35 K to 94 GPa pressure. A search for superconductivity in K to pressures higher than 1 Mbar would thus seem warranted.

In all three heavy alkali metals Cs, Rb, and K the importance of the pressure-induced $s$-$d$ electron transfer has been emphasized. It is likely responsible for the transition from tetragonal $tI4$ to the lower-symmetry orthorhombic $oC16$ structure. McMahon [28] has calculated the completion pressure for the $s$-$d$ transfer in Cs and Rb to be 15 and 53 GPa, respectively, near the pressures where the $tI4 \rightarrow oC16$ transition in both cases begins, but also where the resistivity rises steeply and superconductivity appears. A parallel calculation [28] for K finds its $s$-$d$ transfer to complete at ~60 GPa, a lower pressure than that for the $tI4 \rightarrow oC16$ transition.

In summary, a superconducting transition $T_c$ near 2 K has been observed in four-point electrical resistivity measurements on Rb for pressures above 55 GPa. The transition only occurs after Rb enters the orthorhombic $oC16$ phase which is marked by a sharp increase in the resistivity, $T_c$ decreases under pressure at the rate $-39$ mK/GPa. In all respects these results parallel those found for Cs near 12 GPa pressure. Based on these results it is predicted that K will become superconducting near 1 Mbar pressure when it enters the same $oC16$ phase.

The authors would like to thank G. Fabbris for helpful comments on this manuscript. This research is supported by the National Science Foundation (NSF) through Grants No. DMR-1104742 and No. DMR-1505345 as well as by the Carnegie/DOE Alliance Center (CDAC) through NNSA/DOE Grant No. DE-FC52-08NA28554.
Until 1970 no alkali metal was known to be superconducting. When Wittig [1] applied approximately 12 GPa pressure to Cs in a resistivity experiment, he discovered superconductivity at a temperature $\sim 1.5$ K that decreased under pressure. A few years later a student of Wittig, K. Ullrich [2, 3], found superconductivity in Cs near 50 mK at a lower pressure 11.5 GPa, the value of $T_c$ jumping suddenly from 150 mK to $\sim 1.3$ K at 12.5 GPa as a result of a structural phase transition from Cs-IV ($tI_4$) to Cs-V ($oC_{16}$) [4]. To our knowledge pressure-induced superconductivity in Cs has yet to be confirmed by a second group.

Fig 1S shows the results of the present high-pressure experiments on pure Cs metal using a cryostat capable of cooling from ambient to 1.35 K temperatures. Whereas no superconductivity is observed at 13.6 GPa, at 15.1 GPa a clear resistance drop is observed that shifts to lower temperatures at the higher pressure 16.3 GPa. The resistance in the normal state at 2 K is seen to increase with pressure.

In Fig 2S the resistive transition at 16.3 GPa is seen to shift to lower temperatures with increasing magnetic field to 96 G. A similar result is obtained at 15.1 GPa from which the critical field at 0 K can be estimated $H_o \simeq 270$ G (see main paper). The present results thus confirm the superconducting state in Cs under pressure first observed by Wittig [1] nearly 50 years ago.

In the upper left panel of Fig 3S the present $T_c$ values for superconducting Cs are compared to those from earlier studies by Wittig [1] and his group [2, 3]. The agreement is as close as could be expected in view of the uncertainties in pressure determination between the ruby manometer used here and the superconducting Pb manometer in Wittig’s experiments.

The lower left panel of Fig 3S shows the pressure-dependent resistance of Cs at room temperature. As pointed out earlier [2, 3], the $tI_4 \rightarrow oC_{16}$ phase transition is accompanied by a steep climb in the resistance. In high-pressure synchrotron x-ray diffraction experiments to 13 GPa, Fabbris et al. [8] have shown that the phase boundary between these two Cs phases shifts from $\sim 10$ GPa at room temperature to at least 13 GPa at 10 K. For this reason the phase boundary in the upper left panel has been shifted to the right compared to the lower left panel.
FIG. 3. (color online) (left/upper) \( T_c \) of Cs versus pressure to 17 GPa: present data (■, filled diamond), data from Ref [1] (○), data from Ref [2, 3] (▲, dotted line). All \( T_c \) values determined from midpoint of transition. Solid and dashed lines are guide to eye. Values of slope in mK/GPa in \( oC_{16} \) phase: \(-116\) (dotted line), \(-103\) (solid line), \(-30\) (dashed line). (left/lower) Resistance versus pressure: present data (■), solid line is guide to eye. Structures at top of lower graph determined at 295 K (see Ref [6]). (right/upper) \( T_c \) of Rb versus pressure to 92 GPa from Fig 6 in manuscript. Present data in two separate experiments (●, ■). Solid straight line has slope \( dT_c/dP \approx -39\) mK/GPa. (right/lower) Present data (■). Solid black and red lines are guide to eye. Arrows give direction of measurement. Structures at top of lower graph determined at 295 K (see Ref [7]). In all four graphs, vertical solid blue line separates tetragonal \( tI_4 \) phase from \( oC_{16} \) phase.

Panel to match the pressure where the jump in \( T_c \) occurs (see dotted lines). Notable is then that one of the early \( T_c \) values of Wittig [1] and of the present experiment (diamond) lie to the left of this phase boundary, even though both are almost certainly in the \( oC_{16} \) phase. This apparent discrepancy is a reflection of the difficulty to obtain precise values of the pressure at low temperatures.

Taken together these results show that the \( oC_{16} \) phase favors both superconductivity and higher values of the resistivity. Both effects point to stronger electron-phonon coupling in the \( oC_{16} \) structure.

The two right panels of Fig 3S are taken from Figs 2 and 6 of the main paper. Here the low-temperature phase boundary of Rb between the \( tI_4 \) and \( oC_{16} \) phases at 48.5 GPa has been arbitrarily shifted by \( \sim 5 \) GPa to higher pressures. The synchrotron x-ray measurements by Fabbris et al. [8] were restricted to pressures less than 25 GPa.

Also for Rb the two right panels are consistent with the appearance of superconductivity and a steep climb in the resistance in the \( oC_{16} \) phase. One would expect a similar result for the neighboring heavy alkali metal K where the transition to the \( oC_{16} \) structure doesn’t occur until 96 GPa [9]. Debessai [10] failed to observe superconductivity in K above 1.3 K for pressures up to 94 GPa. It would seem quite likely that a modest extension of this pressure range to somewhat over 1 Mbar would reveal a superconducting ground state for K. Since K is lighter than Rb, the value of \( T_c \) for K would likely be somewhat higher, as for Rb and Cs. Were superconductivity to be discovered in K, that would leave only Na as the sole non-superconducting alkali. It may be difficult to observe superconductivity in this alkali since the \( oC_{16} \) structure has not been found in Na to pressures as high as 2 Mbar [11].