Superconductivity at 17 K in Yttrium Metal under Nearly Hydrostatic Pressures to 89 GPa

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Abstract

In an experiment in a diamond anvil cell utilizing helium pressure medium, yttrium metal displays a superconducting transition temperature which increases monotonically from $T_c \simeq 3.5$ K at 30 GPa to 17 K at 89.3 GPa, one of the highest transition temperatures for any elemental superconductor. The pressure dependence of $T_c$ differs substantially from that observed in previous studies under quasihydrostatic pressure to 30 GPa. Remarkably, the dependence of $T_c$ on relative volume $V/V_0$ is linear over the entire pressure range above 33 GPa, implying that higher values of $T_c$ are likely at higher pressures. For the trivalent metals Sc, Y, La, Lu there appears to be some correlation between $T_c$ and the ratio $r_a/r_c$ of the Wigner-Seitz radius to the ion core radius.
Before the advent of high-temperature superconductivity in 1986, the highest known values of the superconducting transition temperature were exhibited by the binary A-15 compounds V$_3$Si, Nb$_3$Sn and Nb$_3$Ge with $T_c$'s in the range 17 - 23 K [1]. With the discovery in 2001 of superconductivity in MgB$_2$, the highest value of $T_c$ for a binary compound was extended to 40 K [2]. For elemental superconductors, on the other hand, the maximum value of $T_c$ at ambient pressure is only 9.5 K for Nb. Under high pressure conditions, however, the number of elemental superconductors not only increases from 29 to 52 [3, 4, 5], but the transition temperatures for a number of elements (Li, P, S, Ca, V, La) reach values in the range 13 - 20 K formerly “reserved” for the A-15 compounds [6].

In this paper we focus our attention on the four closely related $d$-band metals Sc, Y, La, and Lu which share the trivalent valence electron configuration $nd^1(n+1)s^2$, where $n = 3, 4$ or 5. Whereas La is superconducting at ambient pressure, Sc, Y, and Lu only superconduct under high pressure, all four elements exhibiting a positive pressure derivative $dT_c/dP > 0$ [7, 8, 9, 10]. Some light on the origin of these and other interesting results was shed by the observation of Johansson and Rosengren [11] in 1975 that the ratio of the Wigner-Seitz radius to ionic radius, $r_a/r_c$, appears to play an important role in determining the pressure dependence of the superconducting properties of Y, La, Lu and La-Y, La-Lu alloys as well as the equilibrium crystal structure sequence (hcp $\rightarrow$ Sm-type $\rightarrow$ dhcp $\rightarrow$ fcc) across the rare-earth series. Duthie and Pettifor [12] subsequently demonstrated that these and other important correlations are a consequence of the fact that the ratio $r_a/r_c$ is inversely related to the $d$-band occupancy $n_d$, a quantity which in general increases under pressure due to $s \rightarrow d$ transfer. Later studies show that yttrium metal follows the structure sequence (hcp $\rightarrow$ Sm-type $\rightarrow$ dhcp $\rightarrow$ trigonal) as the applied pressure is increased to 50 GPa at ambient temperature [13, 14]. Melsen et al. [15] have predicted that at pressures above 280 GPa yttrium should transform into the bcc structure. It would be of great interest to extend the above superconductivity/structural experiments to much higher pressures to allow a critical assessment of possible correlations with the ratio $r_a/r_c$ over a wide range of parameters.

Yttrium metal does not superconduct above 6 mK at ambient pressure [7]. However, in 1970 Wittig [16] discovered superconductivity in Y at $T_c \simeq 1.3$ K under 11 GPa quasihydrostatic pressure (solid steatite pressure medium); $T_c$ increases monotonically with pressure at the rate $dT_c/dP \simeq +0.35$ K GPa$^{-1}$, finally reaching 9 K at 30 GPa. In the present paper we extend these earlier studies to much higher pressures; we also provide for a nearly hydrostatic pressure environment by using dense helium as pressure medium. We find that $T_c$ indeed increases monotonically with pressure, ultimately reaching 17 K at 89.3 GPa. This is one of the highest values of $T_c$ ever observed for an elemental superconductor; values above 20 K appear likely at higher pressures. Comparing the pressure dependences for Y, Lu, La, and Sc, the simple inverse relation between $T_c$ and the ratio $r_a/r_c$ proposed by Johansson and Rosengren [11] is found to extend to much higher pressures.
High pressures were generated using a diamond anvil cell (DAC) made of CuBe alloy, nonmagnetic CuBe being used in the critical region near the sample [17]. Two opposing 1/6-carat type IIa diamond anvils with 0.3 mm dia culet and 3 mm table were used. A miniature Y sample was cut from an ingot (Aldrich Chemical 99.9%) to approximate dimensions 60 × 60 × 20 µm³ and placed in a 150 µm dia hole electro-spark-drilled through the center of a 3 mm dia × 250 µm thick gold-plated rhenium or NiCrAl-alloy gasket preindentet to 50 µm (see Fig 1 in Ref [18]). The rhenium gasket used in experimental runs A and B becomes superconducting near 3.5 K under pressure [18, 19], thus allowing the detection of the superconducting signal from the Y sample only for Tc ≥ 4 K. For this reason a nonsuperconducting gasket made of NiCrAl-alloy was used in run C.

Tiny ruby spheres [20] allow the determination [21] of the pressure in situ with resolution ± 0.2 GPa at 20 K. For the results shown here, the standard ruby calibration in Ref [21] was used; however, we point out that Holzapfel [22] has very recently published a revised ruby pressure calibration to 300 GPa which deviates significantly (> 5%) from the previous calibration in the pressure range above 60 GPa. According to this revised ruby scale our highest pressure should be corrected upwards from 89.3 GPa to 96 GPa.

At the beginning of the experiment, the gasket hole is filled with superfluid liquid helium at temperatures below 2 K before sealing it shut by pressing the opposing diamond anvils further into the preindentet gasket. Pressure is changed in the temperature range 150 - 180 K. To reduce the chance of helium penetration into the diamond anvils, the DAC was kept at temperatures below 180 K during the entire duration (∼ 10 days) of each of the three experimental runs.

The superconducting transition is determined inductively using two balanced primary/secondary coil systems connected to a Stanford Research SR830 digital lock-in amplifier. The ac susceptibility studies were carried out using a 3 G (r.m.s.) magnetic field at 1000 Hz. As seen in Fig 1 for the data in run B, the real-part of the ac susceptibility signal changes abruptly at the superconducting transition by 1-2 nV. The relatively low noise level (∼ 0.2 nV) is achieved by appropriate signal compensation and impedance matching as well as through both the use of a long time constant (30 s) on the lock-in amplifier during very slow (100 mK/min) temperature sweeps and the averaging of multiple measurements. Further experimental details of the DAC and ac susceptibility techniques are published elsewhere [17, 23].

In Fig 2 the value of Tc from the transition midpoint is plotted versus pressure for all three experimental runs, revealing excellent agreement. Normally Tc is measured for increasing pressure; however, at the end of run A the pressure was reduced from 48 to 38 GPa (pt 7 to pt 8), demonstrating the reversibility of the pressure dependence Tc(P), at least in this pressure range. The present results, which were obtained under nearly hydrostatic pressure conditions, are seen to differ significantly from those obtained earlier under quasi-hydrostatic pressure conditions where a solid (steatite) was used as pressure medium [16, 9]. Abrupt changes in the slope dTc/dP near 12 and
25 GPa in the earlier data, and at 30-35 GPa in the present data, may be related to the structural transitions reported near 15 GPa ($hcp \rightarrow$ Sm-type) and 30 GPa (Sm-type $\rightarrow$ $dhcp$) at ambient temperature [13, 14]. Note that these phase boundaries may shift upon cooling from ambient to low temperatures.

In Fig 3 we replot the present results from Fig 2 as $T_c$ versus relative volume $V/V_o$ using the equation of state for Y determined by Grosshans and Holzapfel [14]. Remarkably, over the entire pressure range 33 to 89.3 GPa, $T_c$ is seen to be a linear function of the sample volume $V$. Were this linear dependence to continue, the transition temperature $T_c$ would reach values of 20, 25, or 30 K for pressures of approximately 130, 250, or 540 GPa, respectively.

We now explore in Fig 4 whether the observed increase in $T_c$ with pressure for the four trivalent elements Sc, Y, La, and Lu is correlated with the ratio $r_a/r_c$, as originally proposed by Johansson and Rosengren [11], where $r_a = \sqrt[3]{(3/4\pi)V_a(P)}$, $V_a(P)$ is the volume per atom at the given pressure [14, 24], and the ionic radius $r_c$ [24] is assumed independent of pressure. In examining the data in Fig 4 one should keep in mind that the results of quasihydrostatic pressure studies (solid or dashed lines) are included together with those of nearly hydrostatic studies (symbols). That the two very different pressure environments can have a strong influence on the measured $T_c(P)$ dependences is evident from the results on Y in Figs 2 or 4. In addition, the results on La of Tissen et al. [10] using methanol-ethanol pressure medium differ from the earlier, less hydrostatic studies [9].

In spite of these caveats, however, two simple systematics are evident in Fig 4. Firstly, the three nonsuperconducting metals Y, Lu, and Sc become superconducting if high pressure is applied, $T_c$ generally increasing with pressure (decreasing ratio $r_a/r_c$) for all four metals. Secondly, the value of $T_c$ does not increase above 1 K unless the applied pressure is sufficient to bring the ratio down to values below $r_a/r_c \approx 2.1$. For La at ambient pressure the ratio $r_a/r_c$ is clearly less than 2.1; this is consistent with the fact that La’s $dhcp$ phase is superconducting at $T_c \approx 5$ K and its $fcc$ phase at 6 K. It would be interesting to investigate possible correlations between $T_c$ and the ratio $r_a/r_c$ for Sc, Y, La, and Lu to nearly hydrostatic (dense He) pressures well above 100 GPa (1 Mbar) and, in particular, to determine for what value of $r_a/r_c$ the transition temperature $T_c$ passes through its maximum value $T_c^{max}$. The value of $T_c^{max}$, and the pressure (or ratio $r_a/r_c$) at which it occurs, may depend on the degree of hydrostaticity of the pressure medium used.

The value of the superconducting transition temperature found here for Y under 89.3 GPa nearly hydrostatic (dense He) pressure, $T_c \approx 17$ K from the midpoint of the magnetic susceptibility transition, is among the highest ever reported for an elemental superconductor. Using the same susceptibility-midpoint criterium, Ishizuka et al. [25] report that $T_c \approx 16.5$ K for vanadium under 120 GPa nonhydrostatic pressure (no pressure medium), with a superconducting onset at 17.2 K. The superconducting onset in the susceptibility of sulfur takes on a value as high at 17 K at 157 GPa nonhydrostatic pressure [26]. Values of $T_c \approx 18$ K (30 GPa) and 20 K (48 GPa) have...
been, respectively, reported for Ca and Li from their resistivity onsets by Shirotani et al. [27] and Shimizu et al. [28] for nonhydrostatic pressure; however, it is well known that the temperature of the resistivity onset may lie significantly higher than the bulk value of $T_c$ [29]. Subsequent magnetic susceptibility experiments on Li report $T_c^\text{max} \simeq 16$ K (transition onset) at 33 GPa [30] and $T_c^\text{max} \simeq 14$ K (transition midpoint) at 30 GPa [18]. Clearly the value of $T_c$ depends to some extent on the measurement technique and $T_c$-criterion used. In any case, the highest reported values of $T_c$ for elemental superconductors under extreme pressure lie near 17 K. It is interesting to note that for the elements Ca [27], Y, Lu [7], Sc [8], V [25], B [31], S [26], and P [32] the transition temperature $T_c$ is still climbing for the highest pressures reached. It is very likely that in the near future the transition temperature of one of these elemental superconductors will surpass the $T_c = 20$ K barrier under extreme pressures.

To our knowledge, no electronic structure calculation of $T_c$ has yet been carried out for Y at reduced lattice parameters. Such a calculation for V to 945 GPa is in quite good agreement with the experimental results to 120 GPa and predicts that $T_c$ should pass through a maximum value of 21 K at 139 GPa [33]. In view of the linear dependence of $T_c$ on $V/V_o$ to the highest pressure (see Fig 3), it would be of particular interest to carry out a similar calculation for Y.

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Figure Captions

Fig. 1. Real part of the $ac$ susceptibility signal in nanovolts versus temperature for yttrium metal at 14 different pressures from 33 to 89.3 GPa (run $B$). The applied $ac$ field is 3 G (r.m.s.) at 1,000 Hz. Data at different pressures are shifted vertically for clarity. The 1-2 nV jump in the $ac$ susceptibility marks the superconducting transition at $T_c$. As the pressure increases, $T_c$ is seen to increase monotonically.

Fig. 2. Symbols give superconducting transition temperature of yttrium metal versus nearly hydrostatic (dense helium) pressure to 89.3 GPa in present experiments. Error bar gives transition width. Numbers give order of measurements in run $A$; in runs $B$ and $C$ pressure increases monotonically. Solid lines give $T_c(P)$ under quasihydrostatic pressure to 16 GPa from Ref [16] and to 30 GPa from Ref [7].

Fig. 3. Results of present experiments in Fig 2 replotted as $T_c$ versus relative volume $V/V_o$ using equation of state from Ref [14]. Straight line is drawn to emphasize the linear dependence for data above 33 GPa: $T_c(K) = 43.8 - 59.2(V/V_o)$.

Fig. 4. Value of $T_c$ versus ratio of Wigner-Seitz radius to trivalent ionic radius, $r_a/r_c$, for present nearly hydrostatic data on Y from Fig 2 (symbols) as well as for less hydrostatic data on Y [7] and Sc [8] (solid lines), on La [9] and Lu [7] (dashed lines), and on La from Ref [10] (dot-dashed lines). At ambient pressure the value of the ratio $r_a/r_c$ is [21]: Y (2.21), Lu (2.23), Sc (2.45), and La (2.08).
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