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Superconductivity at 17 K in yttrium metal under nearly hydrostatic pressures up to 89 GPa

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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_o is nearly 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, and 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.

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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_3Si, Nb_3Sn and Nb_3Ge 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,[3–5] but the transition temperatures for a number of elements (Li, P, S, Ca, V, and La) reach values in the range of 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 $dT_c/dP > 0$.[7–10] 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 [hexagonal close packed (hcp) → Sm-type → dhcp → face centered cubic (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 $s \to d$ transfer. Later studies show that yttrium metal follows the structure sequence (hcp → Sm-type → dhcp → 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 body-centered-cubic 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 increased 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 diameter culet and 3 mm table were used. A miniature Y sample was cut from an ingot (Aldrich Chemical 99.9%) to approximate dimensions $60 \times 60 \times 20$ μm^3 and placed in a 150 μm diameter hole electrospark drilled through the center of a 3 mm diameter $\times 250$ μm thick gold-plated rhenium or NiCrAl-alloy gasket preindented 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 $T_c \geqslant 4$ 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 to facilitate comparison with previous work. However, we point out that Holzapfel[22] has very recently published a

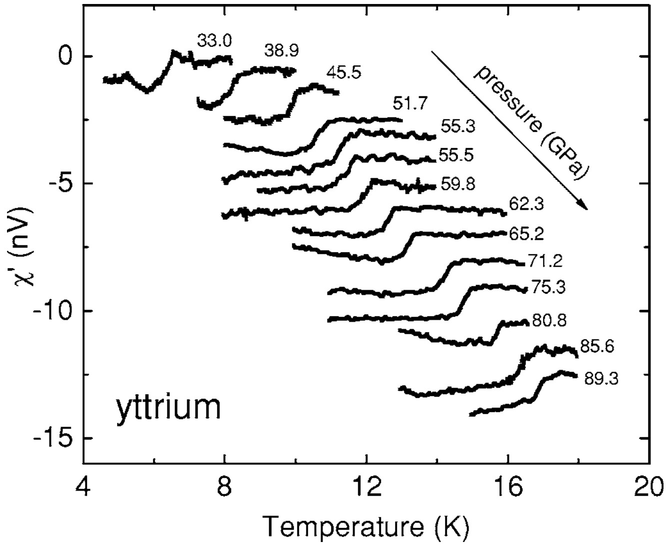

FIG. 1. Real part of the ac susceptibility signal in nanovolts versus temperature for yttrium metal at 14 different pressures from 33 to 89.3 GPa (run *B*). The applied ac field is 3 G (rms) at 1023 Hz. Data at different pressures are shifted vertically for clarity. The 1–2 nV jump in the ac susceptibility marks the superconducting transition at T_c. As the pressure increases, T_c is seen to increase monotonically.

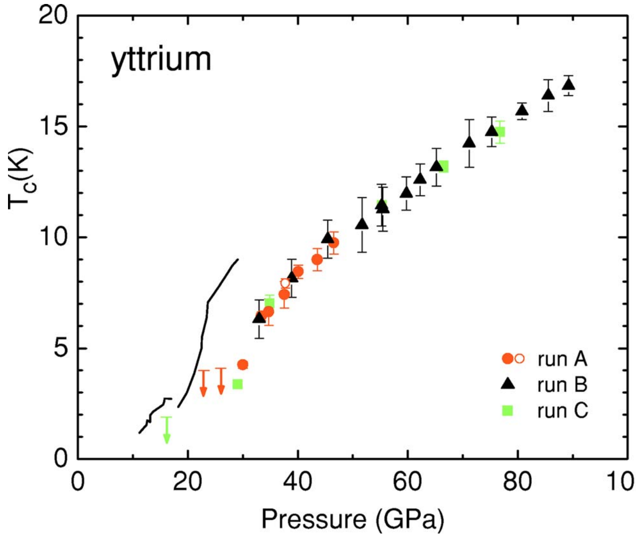

FIG. 2. (Color online) Symbols give superconducting transition temperature of yttrium metal versus nearly hydrostatic (dense helium) pressure to 89.3 GPa in present experiments. Error bars give transition widths. Data (runs *A*,*B*,*C*) taken with increasing pressure except for final point (open red circle) in run *A*. Vertical arrows for $P<30$ GPa indicate the absence of superconductivity above lowest temperature measured (4 K in run *A* or 2 K in run *C*). Solid lines give $T_c(P)$ under quasihydrostatic pressure to 16 GPa (from Ref. 16) and to 30 GPa (from Ref. 7).

revised ruby pressure calibration to 300 GPa which deviates by 5% or more from the previous calibration[21] in the pressure range above 60 GPa. According to this revised ruby scale, our highest pressure should be corrected upward from 89.3 GPa to 96 GPa, but the basic conclusions reached in this paper remain unaffected.

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 preindented 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 located immediately outside the metal gasket and connected to a Stanford Research SR830 digital lock-in amplifier. The ac susceptibility studies were carried out using a 3 G root-mean-square magnetic field at 1023 Hz. As seen in Fig. 1 for the data in run *B*, the real part of the ac susceptibility signal changes abruptly by 1–2 nV at the superconducting transition. 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 T_c from the transition midpoint is plotted versus pressure for all three experimental runs, revealing excellent agreement. Normally T_c is measured for increasing pressure; however, at the end of run *A* the pressure was reduced from 48 to 38 GPa (open red circle), demonstrating the reversibility of the pressure dependence $T_c(P)$, 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 for $P \leq 30$ GPa under quasihydrostatic pressure conditions where the solid steatite was used as pressure medium;[9,16] at 25 GPa, for example, $T_c \simeq 7$ K in the quasihydrostatic measurements, whereas $T_c < 4$ K in the present study. Abrupt changes in the slope dT_c/dP near 12 and 25 GPa in the quasihydrostatic data, and at 30–35 GPa in the present data, may be related to the structural transitions reported near 15 GPa (hcp→Sm-type) and 30 GPa (Sm-type→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 nearly linear function of the sample volume V. Extending the straight-line fit to higher pressures, the transition temperature T_c would reach values of 20, 25, or 30 K for $P \approx 130$, 250, or 540 GPa, respectively. The data in Fig. 3, however, can be somewhat more accurately fit by a quadratic expression with a small positive curvature (dashed line) or by two straight lines (not shown) with slightly different slopes which intersect at $V/V_o \simeq 0.55$ (~53 GPa). One could speculate that such a slope change might be related to the dhcp→trigonal transition seen in structural studies on Y.[13,14]

We now explore in Fig. 4 whether the observed increase

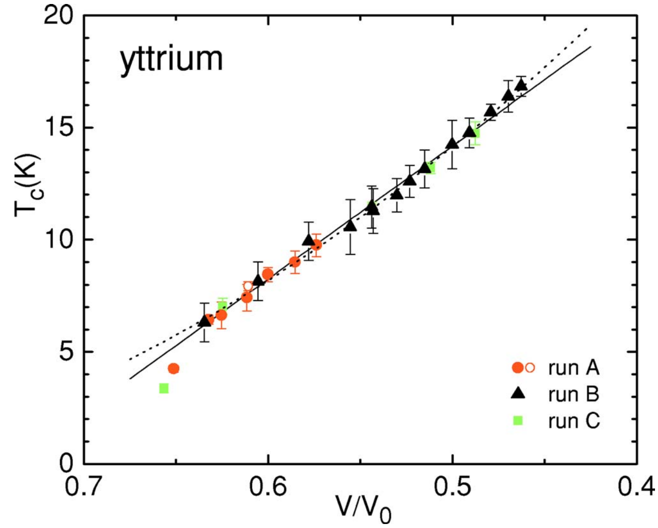

FIG. 3. (Color online) Results of present experiments in Fig. 2 replotted as T_c vs relative volume V/V_o using equation of state (from Ref. 14). Straight line is: $T_c(\mathrm{K})=43.8-59.3(V/V_o)$; dashed line with slight positive curvature is: $T_c(\mathrm{K})=66.1-141(V/V_o)+73.6(V/V_o)^2$.

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 (Ref. 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, dotted, or dashed lines) are included together with those of the present nearly hydrostatic studies (symbols). The fact 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 Fig. 2. In addition, the results on La of Tissen *et al.*[10] in Fig. 4 using methanol-ethanol pressure medium differ from the earlier, less hydrostatic studies.[9]

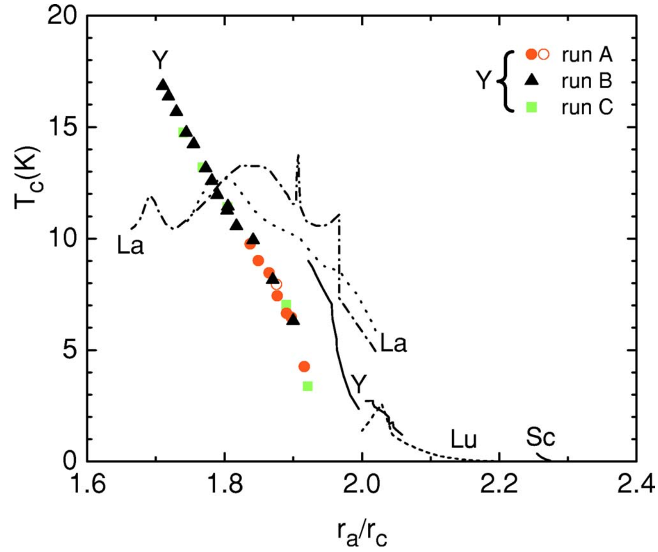

FIG. 4. (Color online) Value of T_c vs ratio of Wigner–Seitz radius to trivalent ionic radius, r_a/r_c, for present nearly hydrostatic data on Y from Fig. 2 (symbols) as well as for less hydrostatic data on Y (Ref. 7) and Sc (Ref. 8) (solid lines), on La (Ref. 9) and Lu (Ref. 7) (dashed lines), and on La (from Ref. 10) (dot-dashed lines). At ambient pressure the value of the ratio r_a/r_c is: Y (2.21), Lu (2.23), Sc (2.45), and La (2.08) (Ref. 24).

In spite of these caveats, two simple systematics are evident in Fig. 4. First, 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. Second, 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 $r_a/r_c \simeq 2.1$. 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 $T_c \simeq 5$ 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, $T_c \simeq 17$ K from the midpoint of the magnetic susceptibility transition, is among the highest ever reported for an elemental superconductor. Using the same susceptibility-midpoint criterion, Ishizuka *et al.*[25] report that $T_c \simeq 16.5$ 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 passes through a maximum value of 17 K near 200 GPa nonhydrostatic pressure.[26] Values of $T_c \approx 18$ K (30 GPa) and 20 K (48 GPa) have been, respectively, reported for P 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 $T_c^{\max} \simeq 16$ K (transition onset) at 33 GPa (Ref. 30) and $T_c^{\max} \simeq 14$ 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,[31], Y, Lu,[7] Sc,[8] V,[25] B,[32] and P,[27] the transition temperature T_c is still climbing for the highest pressures thus far 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 nearly 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.

Note added in proof. We have very recently extended the pressure range of our studies on Y metal to approximately 115 GPa (1.15 Mbar) giving $T_c=19.5$ K (midpoint) and 20.0 K (onset). To our knowledge, this is the highest transition temperature ever measured in the magnetic susceptibility for an elemental superconductor, equaling the value of T_c reported in Ref. 28 for Li from the resistivity onset.

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