Superconductivity at 20 K in Yttrium Metal at Pressures Exceeding 1 Mbar

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Abstract

In experiments in a diamond anvil cell, yttrium metal is found to display a superconducting transition temperature in the ac susceptibility which increases monotonically from 3.5 K at 30 GPa to 19.5 K at 115 GPa, where the transition onset lies at 20 K. This is the second highest value of T_c ever observed for an elemental superconductor. A fit to the Y data using the McMillan equation is consistent with electron-phonon superconductivity with moderately strong coupling.

The trivalent transition metal yttrium does not superconduct at ambient pressure down to temperatures as low as 6 mK [1]. In 1970 Wittig [2] discovered superconductivity in Y with $T_c \simeq 1.3$ K under 11 GPa quasi-hydrostatic 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 [1]. In a recent paper [3] we extended these earlier studies to much higher pressures using the most nearly hydrostatic pressure medium available, dense helium, and found that T_c indeed increases monotonically with pressure, reaching 17 K at 89.3 GPa. In this paper we report an extension of this work to yet higher pressures using no pressure medium; at 115 GPa we find that T_c reaches a value of 19.5 K (transition midpoint in the ac susceptibility). Remarkably, the dependence of T_c on relative volume V/V_0 is found to be nearly linear over the entire pressure range 33-115 GPa.

The diamond anvil cell used contains two opposing 1/6-carat, type Ia diamond anvils with culets beveled from 0.35 mm to 0.18 mm diameter (bevel angle of 7 degrees) and a 3 mm diameter table. A miniature Y sample is cut from an ingot (Aldrich Chemical 99.9%) and placed in an 80 μm diameter hole electro-spark drilled through the center of a gold-sputtered rhenium gasket 3 mm diameter by 250 μm thick and preindented to 32 μm thickness. Tiny ruby spheres [4] are placed next to the Y sample to allow the determination [5] of the pressure *in situ* with resolution ± 0.2 GPa at 20 K. To facilitate comparison with previous work, the standard ruby calibration in Ref. [5] is used. However, we point out that both Holzapfel *et al.* [6] and Chijioke *et al.* [7] have recently published revised ruby pressure calibrations to at least 150 GPa, both of which would revise our highest pressure upwards from 115 GPa to $\sim$ 124 GPa. Whichever calibration is used, the basic conclusions reached in this paper remain unaffected.

At the beginning of the experiment, the Y sample and ruby spheres are placed in the gasket hole with no pressure medium and pressure is applied at room temperature until the gasket hole is reduced in size to that of the sample. At pressures between 65 GPa and 115 GPa the diameter of the sample is approximately 45 μm. In this experiment the pressure is always changed at room temperature. The superconducting transition is detected inductively using a balanced primary/secondary coil system connected to a Stanford Research SR830 digital lock-in amplifier; the excitation field for the ac susceptibility studies is 3 G r.m.s. at 1023 Hz. Further experimental details of the DAC and ac susceptibility techniques are published elsewhere [3, 8, 9].

In Fig. 1 we show the ac susceptibility measurements from the present experiment (run D) and, for comparison, run B from the previous nearly hydrostatic measurements. The real part of the ac susceptibility is seen to decrease abruptly by 1-2 nV upon cooling through the superconducting transition. A temperature-dependent background signal $\chi_b'(T)$ has been subtracted from the data; $\chi_b'(T)$ is obtained by measuring the ac susceptibility at pressures too low to induce superconductivity. The relatively low noise level is achieved primarily by averaging multiple measurements. We observed significant broadening of the ruby fluorescence line in run D (no pressure medium) relative to runs A, B and C (dense helium pressure medium), verifying the nonhydrostaticity of the pressure. In spite of this, Fig. 1 shows there is no significant broadening of the transition in the present nonhydrostatic measurements (run D) relative to the nearly hydrostatic measurements with helium pressure medium (run B).

In Fig. 2 we compare the pressure dependence of T_c in the present nonhydrostatic pressure study (run D) to that obtained previously under nearly hydrostatic conditions (runs A, B, C). In all experiments T_c is seen to increase monotonically with pressure. The value of T_c is determined from the transition midpoint in all four runs; the transition midpoint typically lies ~ 0.5 K lower than the transition onset. The present experiment extends the pressure range of the previous studies to 115 GPa; at this pressure the transition midpoint lies at 19.5 K with the onset at 20.0 K. This is the second highest value yet observed for an elemental superconductor, surpassed only by the value $T_c \simeq 25$ K from the resistivity onset recently reported byYabuuchi *et al.* [10] for Ca at 160 GPa. At our highest pressure, 115 ± 5 GPa, the ruby fluorescence line became very broad and weak, resulting in the relatively large uncertainty in our pressure determination for this point, as seen in Fig. 2. After the measurement at 115 GPa, we increased the force applied to the anvils, but T_c did not change; unfortunately, we were no longer able to detect the ruby fluorescence line. Presumably either the applied force did not lead to an increase in pressure in the cell or $T_c(P)$ reached a maximum at these pressures.

There is excellent agreement between the $T_c(P)$ dependences for Y in the three nearly hydrostatic runs A, B, C in Fig. 2. It seems rather remarkable that these dependences agree rather closely with the $T_c(P)$ dependence obtained in the present nonhydrostatic experiment (run D) where no pressure medium was used and the diamond anvils pressed directly onto the Y sample; as pointed out previously [3], there are significant differences between the present $T_c(P)$ dependences and those from earlier studies [2] under quasihydrostatic pressure with solid steatite pressure medium.

In Fig. 3 we replot the results from runs A-D in Fig. 2 as T_c versus relative volume V/V_0 using the equation of state for Y given by Grosshans and Holzapfel [11]. Remarkably, the dependence of T_c on relative volume appears nearly linear over the entire pressure range above 33 GPa ($V/V_0 \leq 0.64$). The agreement between all three of our nearly hydrostatic measurements (runs A, B, C) is excellent, however, our nonhydrostatic measurement (run D) appears to exhibit a somewhat greater slope (see figure caption).

We now consider our results in light of the McMillan equation [12, 13]

$$T_c \simeq \frac{\langle\omega\rangle}{1.20} \exp\left[\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right] \tag{1}$$

which is valid for moderately strong electron-phonon coupling ($\lambda \leq 1.5$) and relates T_c to the electron-phonon coupling parameter λ, an average phonon frequency $\langle\omega\rangle$, and a Coulomb repulsion term μ^*. We assume μ^* is independent of pressure and assign $\mu^* = 0.1$. The electron-phonon coupling parameter is given by

$$\lambda = \frac{N\left(E_F\right)\langle I^2\rangle}{M\langle\omega^2\rangle}, \tag{2}$$

where $\eta \equiv N\left(E_F\right)\langle I^2\rangle$ is the Hopfield parameter [14] given by the product of the electronic density of states and the average-squared electronic matrix element and M is the ionic mass. To explore how T_c can behave under pressure, it remains to find expressions for the volume dependence of $\langle\omega\rangle$ and λ.

Following previous analyses [15, 16], we integrate the definition of the lattice Grüneisen parameter, $\gamma \equiv -d\ln\langle\omega\rangle/d\ln V$, to obtain an expression for the volume dependence of the average phonon frequency

$$\langle\omega\rangle_V = \langle\omega\rangle_{V_0}\left[V/V_0\right]^{-\gamma}. \tag{3}$$

Introducing the parameter $\varphi \equiv \partial\ln\lambda/\partial\ln V$ and integrating, one finds an expression for the volume dependence of the electron-phonon coupling parameter

$$\lambda\left(V\right)=\lambda\left(V_0\right)\left[V/V_0\right]^{\varphi}, \tag{4}$$

where it is easy to show that $\varphi=\partial\ln\eta/\partial\ln V+2\gamma$. The parameter $\partial\ln\eta/\partial\ln V$ is negative and normally lies near -1 for s,p-metals or -3 to -5 for d-metals [17]. Since 2γ is positive, whether λ (and T_c) increases or decreases with pressure depends on whether $|\partial\ln\eta/\partial\ln V|>2\gamma$ or vice versa.

We assign the Grüneisen parameter a value $\gamma=+1.08$ based on an average of the values for Y listed in Ref. [18] and assume that it does not vary with pressure. One can estimate the average phonon frequency using the empirical relation [19] $\langle\omega\rangle\simeq0.69\Theta_D$; for the Debye temperature we use $\Theta_D=244.4$ K from Ref. [20]. Substituting Eqs. 3 and 4 into Eq. 1 and using the experimentally determined values mentioned above, one obtains an expression for the volume dependence of T_c. In the present analysis $\lambda\left(V_0\right)$ and $\partial\ln\eta/\partial\ln V$ are used as fit parameters which, as for γ, are assumed to be independent of pressure. Note that in materials which superconduct at ambient pressure $\lambda\left(V_0\right)$ can be determined directly from Eq. 1 by inserting the ambient-pressure values of T_c and Θ_D. If only one of $\lambda\left(V_0\right)$ or $\partial\ln\eta/\partial\ln V$ is used as a fit parameter, and the other is fixed at some estimated value, a good fit to the data is generally not obtained.

Using the above procedure, we perform two separate fits of the data in Fig. 3, one for the three nearly hydrostatic runs for $V/V_0\geq0.65$ (dashed line in Fig. 4) and one for the nonhydrostatic data (solid line in Fig. 4). For the nearly hydrostatic data we obtain from the fit procedure $\lambda\left(V_0\right)=0.44$ and $\partial\ln\eta/\partial\ln V=-2.90$. For the non-hydrostatic data (run

D) we obtain $\lambda(V_0) = 0.44$ and $\partial \ln \eta / \partial \ln V = -2.87$. Our values for $\lambda(V_0)$ are reasonably consistent with both the value $\lambda(V_0) = 0.3 \pm 0.05$ estimated by Knapp *et al.* [21] by comparing heat-capacity data at high and low temperatures and with theoretical calculations of λ (see, for example, Refs. [22, 23, 24]). Over the pressure range in which we observe superconductivity in Y, this analysis yields values of λ which increase with pressure from 0.6 to 0.8. The above values for $\partial \ln \eta / \partial \ln V$ are close to the range $(-3 \leq \partial \ln \eta / \partial \ln V \leq -5)$ normally found for transition metals [14].

Although the fits using the McMillan equation reproduce the broad features of T_c versus V/V_0, they are not able to reproduce the near linearity of the data; this is especially evident when comparing the linear and McMillan fits of run D in Figs. 3 and 4, respectively. We note that the fit curves shown in Fig. 4 would predict at ambient pressure that $T_c \simeq 1.2$ K, in contrast to experiment where $T_c < 6$ mK [1]. However, several structural phase transitions occur over the pressure range studied [11] so that one would not expect good agreement with data extrapolated to ambient pressure from a high-pressure phase.

The above phenomenological analysis shows that the $T_c(P)$ dependence observed for Y appears consistent with moderately strong-coupled phonon-mediated superconductivity using reasonable values of the averaged parameters. However, to pinpoint the mechanism responsible for the significant increase in T_c with pressure in experiment, detailed electronic structure calculations for Y are clearly needed. Yin *et al.* [25] have very recently carried out such calculations which include pressure-dependent changes in the lattice vibration spectrum. They find a strong pressure-induced increase in the $4d$ content of the occupied conduction electron states and a particularly strong coupling to the transverse phonon branches at high symmetry zone boundary points.

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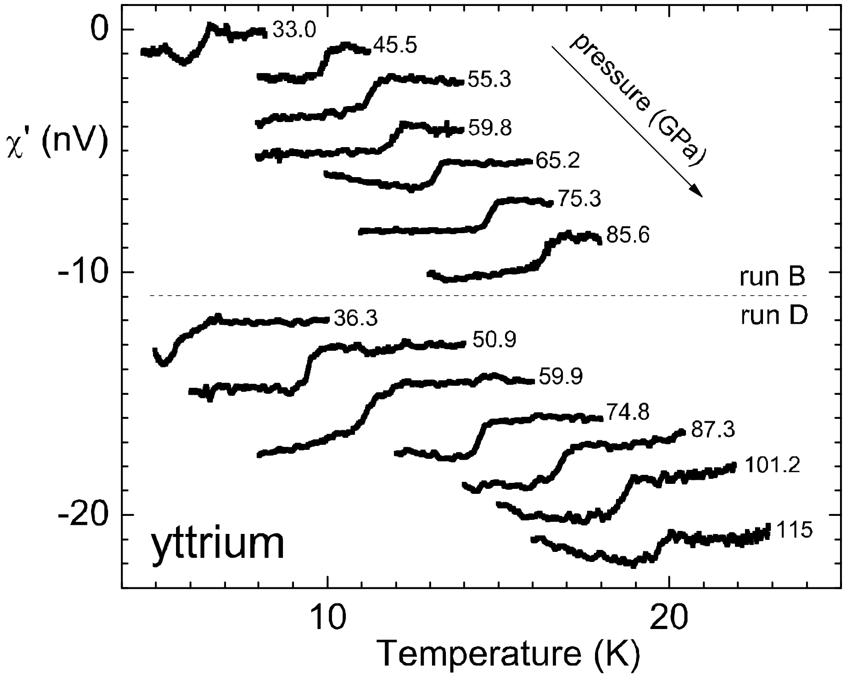

Figure 1. Real part of the ac susceptibility signal in nanovolts versus temperature for yttrium at a variety of different pressures ranging from 33 to 115 GPa. Measurements from run B (Ref. [3]) and D (present experiment) are shown. T_c is seen to increase monotonically with pressure in both runs.

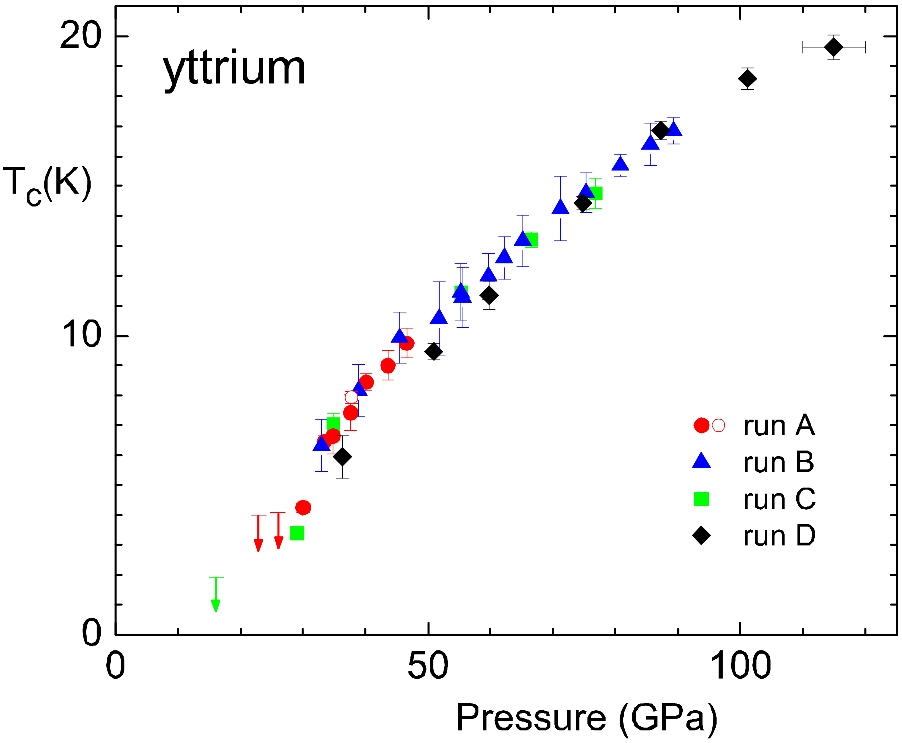

Figure 2. (Color online) Data points give midpoint of the superconducting transition in the ac susceptibility of yttrium metal versus pressure. Vertical error bars represent the width of the transition. Run D is present data; runs A, B, C are from Ref. [3]. Data for all runs taken with increasing pressure except for the final point (open red circle) in run A. Vertical arrows for $P \leq 30$ GPa indicate the absence of superconductivity above lowest measured temperature.

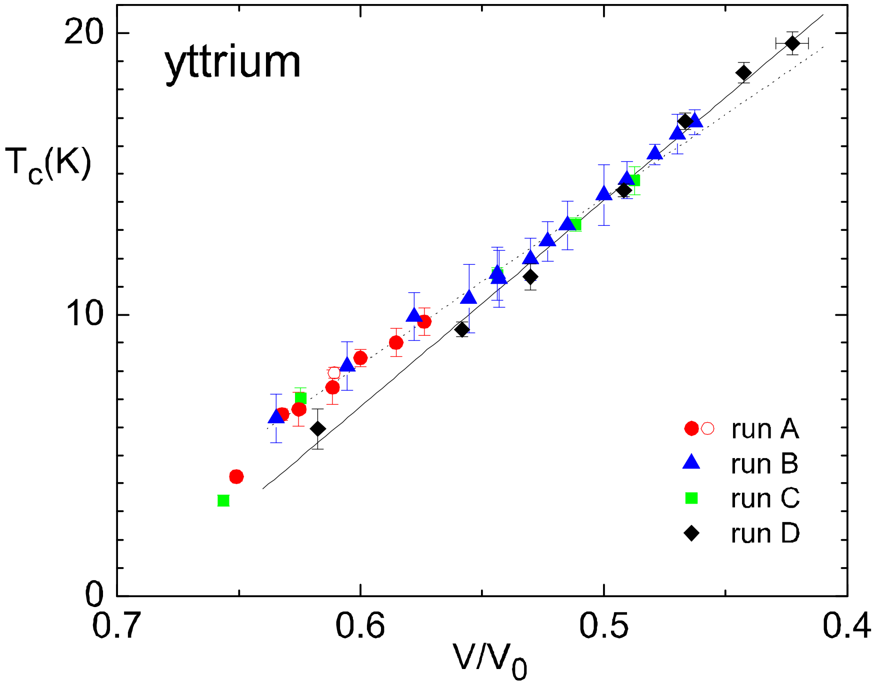

Figure 3. (Color online) Results of experiments in Fig. 2 replotted as T_c versus relative volume V/V_0 (where V_0 is the volume at ambient pressure) using equation of state from Ref. [11]. Data from runs A, B and C from Ref. [3]. Present data to 115 GPa (run D). Solid line given by $T_c(K) = 50.7 - 73.2(V/V_0)$ is a linear fit of all run D data. Dotted line given by $T_c(K) = 43.8 - 59.3(V/V_0)$ is a linear fit of all run A,B,C data (excluding the two lowest pressure data points at $V/V_0 \geq 0.65$).

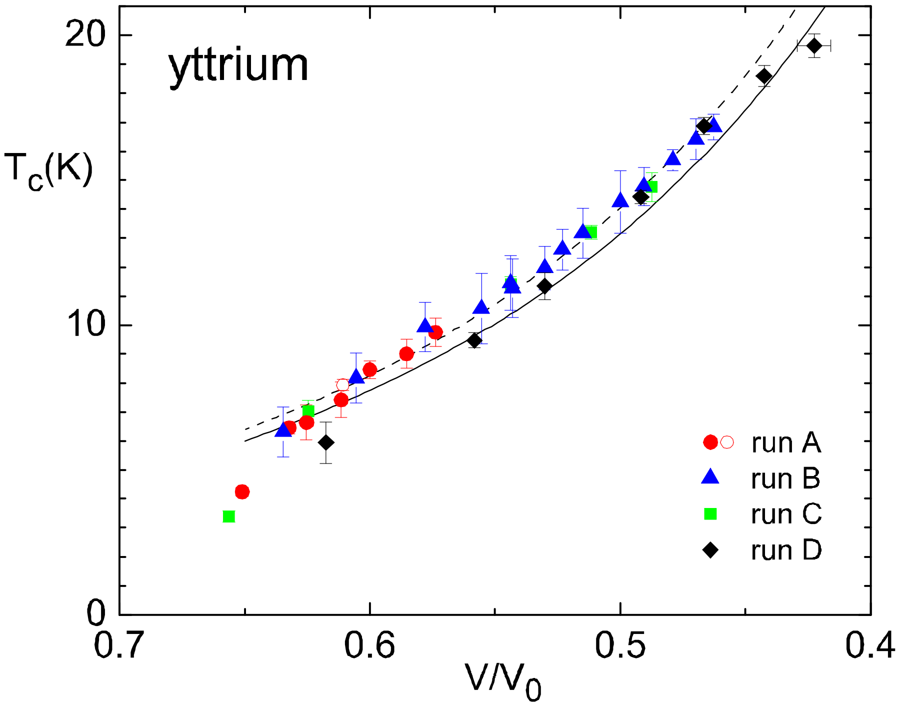

Figure 4. (Color online) Same data as Fig. 3 now shown with the McMillan equation fit curves described in the text. Solid curve is a fit of all run D data. Dotted curve is a fit of all run A,B,C data (excluding the two lowest pressure data points at $V/V_0 \geq 0.65$).