# Pressure-induced superconductivity in Sc to 74 GPa

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Using a diamond-anvil cell with nearly hydrostatic helium pressure medium, we have significantly extended the superconducting phase diagram $T_c(P)$ of Sc, the lightest of all transition metals. We find that superconductivity is induced in Sc under pressure, $T_c$ increasing monotonically to 8.2 K at 74.2 GPa. The $T_c(P)$ dependences of the trivalent $d$-electron metals Sc, Y, La, and Lu are compared and discussed within a simple $s \rightarrow d$ charge transfer framework.

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Even though half a century has passed since the development of a microscopic theory of superconductivity,[1] it is still not possible to reliably calculate values of the superconducting transition temperature $T_c$ for a given material; in fact, one is not even able to reliably predict which materials become superconducting and which do not. One strategy to make progress in this situation is to establish systematics in $T_c$ as a function of composition across alloy and compound series and then test whether a particular theoretical approach is able to account for these systematics. A related strategy is to look for systematics in the dependence of $T_c$ on high pressure in a particular class of materials.[2] This latter "high-pressure" approach has the advantage of being able to track changes in $T_c$ on a single sample but often has the disadvantage of being able to generate only relatively modest changes in $T_c$. The use of the diamond-anvil cell alleviates this problem since, by extending the pressure range to the multimegabar region, it is capable of generating sizable changes in the superconducting properties.

The $T_c(P)$ systematics in the simple-metal superconductors such as Al, In, Sn, and Pb, where the conduction electrons possess $s$, $p$ character, are very simple, namely, $T_c$ always decreases under pressure, i.e., the superconductivity is weakened.[2] The reason for this is that the pressure-induced changes in the lattice vibrations dominate over those in the electronic system, leading to a decrease in $T_c$ as the lattice stiffens under pressure. In such simple-metal systems, it is an interesting physics question to explore the manner in which $T_c$ approaches 0 K as the pressure is increased; pioneering studies in this direction were carried out in the 1970s by Gubser and Webb[3] on superconducting Al by combining diamond-anvil cell, dilution refrigeration, and superconducting quantum interference device detection technology.[4] Such high-pressure investigations at mK and sub-mK temperatures, however, are extraordinarily difficult and require that the materials studied be highly purified to contain only trace concentrations of magnetic impurities.

Rather than use high pressures to *destroy* superconductivity, as in the simple metals, an alternative approach with perhaps greater promise is to use high pressure to *create* superconductivity, i.e., to focus investigations on nonsuperconducting materials which require high pressures to become superconducting. In such studies, not only can the behavior of superconductivity near 0 K be studied but also the maximum attainable value of $T_c$ for a given class of materials can be explored. Of the 52 known superconducting elements, fully 23 only become superconducting if sufficient pressure is applied.[2] Particularly interesting in this regard are the alkali and noble metals, none of which superconduct at ambient pressure. Since they are simple metals, pressure would be expected to weaken the pairing interaction, so they should never become superconducting, no matter how high the pressure. Yet both Cs (Refs. 5 and 6) and Li (Refs. 7–9) do superconduct at sufficiently high pressures, $T_c$ for Li even reaching 15–20 K. Neaton and Ashcroft have shown that the electronic structure of Li (Ref. 10) and Na (Ref. 11) becomes increasingly non-free-electron-like as the volume available to the conduction electrons outside the ion cores rapidly diminishes under very high pressures. Cs, in fact, becomes a transition metal above ~3 GPa as its $5d$ band begins to fill through $s \rightarrow d$ transfer.[12] Similar considerations are expected to apply to the electronic structure of many "simple-metal" materials.[11] In transition metal and rare-earth systems, it has been appreciated for some time that the $d$-electron concentration $n_d$ generally increases under pressure and is mainly responsible for the systematic progression of crystal structures under pressure exhibited by both systems.[13,14]

Superconductivity is most likely to occur in those materials containing one or more nonmagnetic transition metal (or $d$-electron) elements, notable exceptions being the trivalent metals Lu, Y, and Sc. Why are these three elements not superconducting at ambient pressure, whereas isoelectronic La is? The answer may lie in the fact that they simply do not have a sufficient number of $d$ electrons to support superconductivity; La, on the other hand, has more $d$ electrons due to its significantly larger ion core.[13] The assertion that Lu, Y, and Sc have an insufficient $d$-electron count for superconductivity is supported by the fact that all $3d$, $4d$, and $5d$ transition metals in columns IV and V do superconduct at ambient pressure, and those in column V with their greater $d$-electron count have values of $T_c$ roughly 20× higher. Increasing the $d$-electron concentration in Lu, Y, and Sc by applying high pressure would be expected, therefore, to promote superconductivity. Indeed, Wittig *et al.* were the first to show this to be true for Lu,[15,16] Y,[5] and Sc.[17] Whereas in La $T_c(P)$ passes through a maximum near 13 K,[18,19] that for Y continues to increase to the highest pressure applied (≃20K at 1.2 Mbar). $T_c$ for Lu (Ref. 16) and Sc (Ref. 17) also increases under pressure but only reaches values of 2.5 and 0.35 K at 22 and 21.5 GPa, respectively.

 

In this Brief Report, we extend the earlier studies[17] on elemental Sc to much higher pressures. $T_c$ increases monotonically with pressure, reaching 8.2 K at 74.2 GPa. To help illuminate the nature of the superconductivity for all four trivalent metals Sc, Y, Lu, and La, we search for systematics in the dependence of $T_c$ on the free volume fraction available to the conduction electrons.

The diamond-anvil cell used contains two opposing 1/6-carat, type Ia diamond anvils with 0.4 mm diameter culets. A miniature Sc sample ($\sim$70 $\mu$m diameter $\times$35 $\mu$m thick) is cut from a high-purity ingot (99.98% metal basis) obtained from the Materials Preparation Center of the Ames Laboratory[20] and placed in a 180 $\mu$m diameter hole electrospark drilled through the center of a gold-sputtered NiMo gasket 3 mm in diameter by 250 $\mu$m thick and preindented to 45 $\mu$m thickness. Tiny ruby spheres[21] are placed next to the Sc sample to allow the determination of the pressure *in situ* at 20 K with a resolution ±0.2 GPa. We use the revised ruby pressure scale of Chijioke *et al.*[22] The R1 ruby fluorescence line remains sharp up to the highest pressures confirming the near hydrostaticity of the pressure environment in the present experiment.

At the beginning of the experiment, the Sc sample and ruby spheres are placed in the gasket hole. The pressure cell is then placed in a continuous flow cryostat (Oxford Instruments) and submerged in liquid helium. To ensure that no bubbles of gaseous He are trapped inside the gasket, the helium is cooled below the lambda point before sealing the high-pressure volume by pressing the diamonds into the gasket. At the highest pressures, the Sc sample remained completely surrounded by the nearly hydrostatic dense helium pressure medium. To reduce the possibility of He diffusion into the diamond anvils, the temperature was kept below 180 K during the entire experiment. Following the initial compression at 1.6 K, the pressure was only changed between 100 and 180 K.

The superconducting transition is detected inductively using a balanced primary and/or secondary coil system connected to a Stanford Research SR830 digital lock-in amplifier via an SR554 transformer preamplifier; the excitation field for the ac susceptibility studies is 3 Oe rms at 1023 Hz. To facilitate the recognition of the superconducting transition, a temperature-dependent background signal $\chi_b'(T)$ is subtracted from the measured susceptibility data; $\chi_b'(T)$ is obtained by measuring at pressures too low to induce superconductivity. A relatively low noise level is achieved by using the transformer preamplifier to ensure good impedance matching, varying the temperature very slowly (100 mK/min) at low temperatures, using a long time constant (30 s) on the lock-in amplifier, and averaging over two to three measurements. Further experimental details of the high pressure and ac susceptibility techniques are published elsewhere.[23–25]

In Fig. 1, we show the results of the present ac susceptibility measurements for nearly hydrostatic pressures from 54.3 to 74.2 GPa. The real part of the ac susceptibility $\chi'(T)$ decreases abruptly by 3–4 nV upon cooling through the superconducting transition. $T_c$ is seen to increase monotonically with pressure. Signal fluctuations arising from the $^4$He boiling point and superfluid transition prevented the acquisition of reliable data below 4 K. The shift in $T_c \simeq 8.2$ K under an applied dc magnetic field up to 500 Oe was less than the experimental resolution, implying that $|dT_c/dH| \lesssim 0.3$ mK/Oe. Since values of $dT_c/dH$ at low fields for type I superconductors are typically a few mK/Oe, the superconductivity in Sc is likely type II, as in La and Y. For an Y sample with $T_c \approx 9.7$ K at 46.6 GPa,[23] $T_c$ was found to decrease under magnetic fields to 500 Oe at the rate $dT_c/dH \approx -0.5$ mK/Oe.

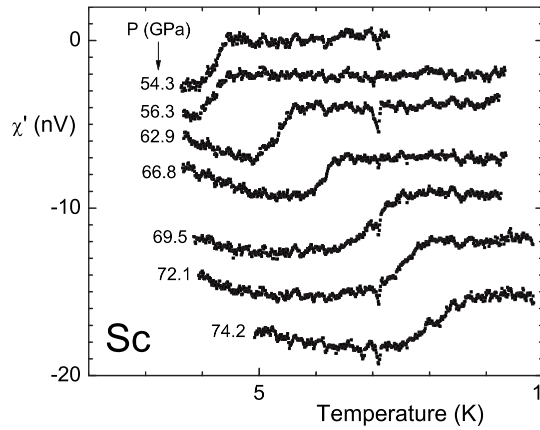


FIG. 1. Real part of the ac susceptibility signal in nanovolts versus temperature for Sc at different pressures ranging from 54.3 to 74.2 GPa. Curves are shifted vertically for clarity. The superconducting transition temperature $T_c$, which is defined by the transition midpoint, is seen to increase monotonically with pressure.

In Fig. 2, the dependence of $T_c$ on pressure for Sc is shown from the present experiment to 74.2 GPa and compared with the previous quasihydrostatic pressure results of Wittig *et al.*[17] to 21.5 GPa. It is worth noting that, in contrast to the results for Y, the dependence of $T_c$ on pressure for Sc exhibits an upward (positive) curvature, in spite of the fact that its compressibility *decreases* with increasing pressure.[29] The accelerating increase in $T_c$ with pressure in Sc gives hope that much higher values of $T_c$ can be reached in future

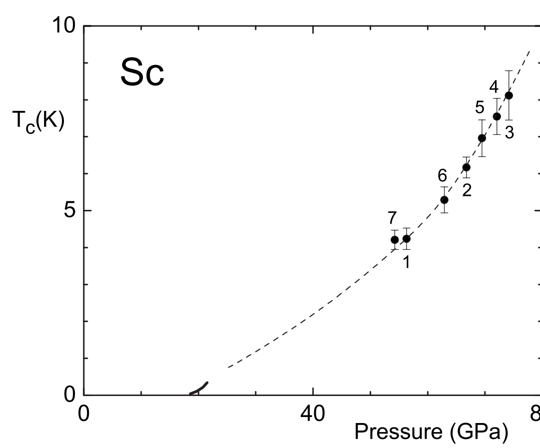


FIG. 2. Superconducting transition temperature $T_c$ versus pressure to 74.2 GPa. Numbers give order of measurement. Dashed line is guide to the eyes and links present data (●) to previous results of Wittig *et al.* to 21.5 GPa (Ref. 17) (short solid line).

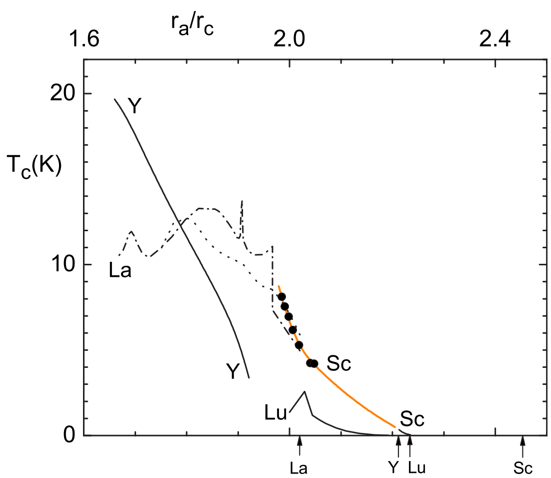


FIG. 3. (Color online) Superconducting transition temperature $T_c$ plotted versus ratio $r_a/r_c$ of Wigner-Seitz to ion core radius for present data on Sc (●) from Fig. 2, Y (solid line) from Ref. 23, Lu (solid line) from Refs. 16 and 18, and La (dotted line from Ref. 18 and dot-dashed line from Ref. 19). Vertical arrows mark values of $r_a/r_c$ for the respective metal at ambient pressure (Ref. 26). See Ref. 26 for full details regarding calculation of pressure dependence of ratio $r_a/r_c$.

experiments in the multimegabar pressure range.

We now compare the change in $T_c$ under pressure from all known high-pressure experiments on Sc, Y, La, and Lu. Instead of simply plotting $T_c$ versus pressure, we plot in Fig. 3 $T_c$ versus the ratio $r_a/r_c$ of the Wigner-Seitz radius $r_a$ to the ion core radius $r_c$.[26] This ratio is directly related to the free volume available to the conduction electrons outside the ion cores; the relative decrease in this free volume under pressure is particularly rapid as the ion cores draw close together and begin to overlap. Johansson and Rosengren[27] were the first to recognize that the ratio $r_a/r_c$ appears to play an important role in characterizing the pressure dependence of $T_c$ in Y, La, Lu and La-Y, and La-Lu alloys as well as in the equilibrium crystal structure sequence across the rare-earth series. Duthie and Pettifor[13] subsequently demonstrated for La and Lu that the correlations in the structure sequence are a consequence of the fact that the $d$-band occupancy $n_d$ increases under pressure due to $s \rightarrow d$ transfer as the equilibrium atomic volume decreases.

Although differing in detail, the $T_c$ versus $r_a/r_c$ data in Fig. 3 for Y, La, Sc, and Lu have important features in common, namely, that as $r_a/r_c$ decreases under pressure, $T_c$ initially rises rapidly, reaching ~3–4 K for values of $r_a/r_c$ between 1.9 and 2.1. The fact that superconductivity in Sc initiates at the relatively large ratio $r_a/r_c \approx 2.24$ fueled our interest in this metal since it suggested to us that sufficient pressure might yield relatively high values of $T_c$. With the exception of Sc, the similarities in the pressure dependences of $T_c$ in Fig. 3 are matched by the similarities in the pressure-induced changes in crystal structure[28,29] which fit in quite well with the well-known hcp→Sm-type→dhcp→fcc structure sequence characteristic for the rare-earth metals. This is not surprising since, with the exception of Eu and Yb, all rare earths are also trivalent $d$-electron metals. Sc falls somewhat out of line since it transforms at ~23 GPa from the hcp to an incommensurate host-guest structure[30,31] instead of to the canonical Sm-type structure. In fact, recent x-ray diffraction experiments on Sc to 297 GPa reveal four successive structure changes, the final being to a new helical chain structure above 240 GPa.[32] It has been suggested that the differences between Sc and the other trivalent $d$-electron metals may arise at least in part from the changes in electronic structure associated with the complete absence of $d$ electrons in Sc's ionic core, thus allowing its 3$d$ valence electrons to penetrate further into the core region (no orthogonality condition) and thus to assume a higher degree of localization.[33,34] The slow monotonic increase in the $E_{2g}$ vibration mode and the $C_{44}$ elastic shear modulus of Sc under pressure are also anomalous.[34]

In Fig. 3, it is seen that the dependence of $T_c$ on $r_a/r_c$ for Sc matches rather well that for La but lies above those for Y and Lu. That the $T_c$ versus $r_a/r_c$ dependences for these four trivalent $d$ metals do not map on top of each other is not surprising. A more relevant parameter for superconductivity than the ratio $r_a/r_c$ might be the number of $d$ electrons per atom in the conduction band $n_d$. For La and Lu under ambient conditions, for example, Duthie and Pettifor[13] estimate that $n_d \simeq 2.5$ and 1.9, respectively. Were the $T_c(P)$ versus $n_d(P)$ dependences for these four elemental metals to fall closely together, this would suggest that the simple $d$-electron count has a particularly close tie to the superconductivity. It is, of course, clear that a detailed understanding of $T_c(P)$ must necessarily take into account pressure-induced changes in crystal structure. However, if we have learned anything in the field of superconductivity, it is that real progress often entails searching for and identifying overriding systematics. The available data from experiment and theory are not yet sufficiently complete that a possible correlation between $T_c$ and $n_d$ can be properly identified. Still needed for this purpose are (1) further $T_c(P)$ data on Y, Lu, and Sc to much higher pressures and (2) an accurate estimate of $n_d(P)$ for all four trivalent $d$ elements from a unified electronic structure calculation.

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