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Comparison of the pressure dependences of T_c in the trivalent *d*-electron superconductors Sc, Y, La, and Lu up to megabar pressures

M. Debessai, J. J. Hamlin, and J. S. Schilling

Department of Physics, Washington University, CB 1105, One Brookings Drive, St. Louis, Missouri 63130, USA

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Whereas double hcp (dhcp) La superconducts at ambient pressure with $T_c \simeq 5$ K, the other trivalent *d*-electron metals Sc, Y, and Lu only superconduct if high pressures are applied. Earlier measurements of the pressure dependence of T_c for Sc and Lu metal are here extended to much higher pressures. Whereas T_c for Lu increases monotonically with pressure to 12.4 K at 174 GPa (1.74 Mbar), T_c for Sc reaches 19.6 K at 107 GPa, the second highest value observed for any elemental superconductor. At higher pressures a phase transition occurs whereupon T_c drops to 8.31 K at 111 GPa. The $T_c(P)$ dependences for Sc and Lu are compared with those of Y and La. An interesting correlation is pointed out between the value of T_c and the fractional free volume available to the conduction electrons outside the ion cores, a quantity which is directly related to the number of *d* electrons in the conduction band.

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I. INTRODUCTION

One of the most important goals in the field of superconductivity is to recognize the properties favorable for pushing the superconducting transition temperature T_c to ever higher values. A material which superconducts at or above room temperature would likely have a lasting impact on current technology. The vast majority of known superconducting materials exhibits T_c's below 10 K, including all elemental superconductors at ambient pressure,[1,2] as seen in Fig. 1. To our knowledge, values of T_c at or above 20 K have been reported only for the cuprate[3] and Fe-based oxides,[4] Nb_3Ge,[5] MgB_2,[6] Rb_3C_{60},[7] possibly Cs_3C_{60},[8] and, under very high pressures, for the elemental metals Ca,[9] Y,[10] and Li.[11] Whereas the high-T_c oxides, which superconduct at temperatures as high as 134 K under ambient conditions ($HgBa_2Ca_2Cu_3O_{8+\delta}$),[12] are generally believed to benefit from a nonphononic pairing interaction,[3] the other members of the above 20K-or-above group likely exhibit conventional electron-phonon pairing. Whatever the nature of the pairing, it is important to establish the conditions favorable for maximizing T_c.

High pressure is a particularly valuable tool for identifying systematics in a given physical phenomenon, such as superconductivity or magnetism, since it generates changes in the physical properties of a single sample in a controlled manner. For example, in a simple-metal superconductor such as Al, In, Sn, or Pb, where the conduction band is made up of *s*,*p* electrons, T_c is always found to *decrease* initially under pressure.[2] In fact, this result was observed for Sn by Sizoo and Onnes in 1925[13] in the first high-pressure experiment ever carried out on a superconductor; they concluded that "… a relatively large space between the atoms is favourable for the appearing of the supraconductive state …." It is, therefore, surprising that dT_c/dP is strongly positive for the simple metals Li (Ref. 14) and Ca (Ref. 9) if they are subjected to pressures in the range above 20 GPa. In superconductors containing transition metals, where *d* electrons dominate the conduction-band properties, T_c can initially rise or fall under pressure and exhibit a highly nonlinear $T_c(P)$ dependence at higher pressures (see, for example, Refs. 15–18). With such complexity in $T_c(P)$ it would seem useful to search for a simple, underlying mechanism to account for the observed changes in T_c as a function of decreasing interatomic spacing as pressure is applied.

More than three decades ago Johansson and Rosengren[19] pointed out an interesting correlation between the crystal structure sequence hcp→Sm-type →dhcp→fcc across the rare-earth series from Lu to La at ambient pressure, or for a given rare-earth metal under increasing pressure, and the increasing fractional atomic volume occupied by the ion core. This correlation was put on a more quantitative footing by Krüger *et al.*[20] through their extensive structural experiments to higher pressures and temperatures. Duthie and Pettifor[21] showed that the observed structural sequence across the rare-earth series both at ambient and high pressure can be quantitatively correlated with the *d*-band occupancy N_d. In fact, the crystal structures across the 3*d*, 4*d*, and 5*d* transition metal series have also been shown to be closely correlated with N_d.[22]

In view of this significant correlation between N_d and crystal structure for *d*-electron metals, it would be interesting to inquire whether other properties, such as the value of the superconducting transition temperature T_c, might also be correlated with the *d*-electron count N_d. As seen in Fig. 1, with the exception of the magnetic (Cr, Mn, Fe, Co, Ni) and nearly magnetic (Pd, Pt) transition metals, all transition-metal elements are superconducting at ambient pressure with transition temperatures ranging from 325 μK for Rh to 9.50 K for Nb.[1,2] The 15 trivalent rare-earth metals La through Lu possess a similar *d*-electron character near the Fermi energy as the beginning transition metals Sc and Y, neither of which is superconducting at ambient pressure. Of the rare earths, only La superconducts at ambient pressure, the remaining, besides Yb and Lu, being magnetic which acts to suppress the superconductivity. We note that an interesting systematics in T_c was uncovered by McMillan[23] for the 5*d*-electron transition metal series; the empirical electronic density of states at the Fermi energy $N(E_f)$ estimated from T_c and specific-heat data was found to track well a calculated ca-

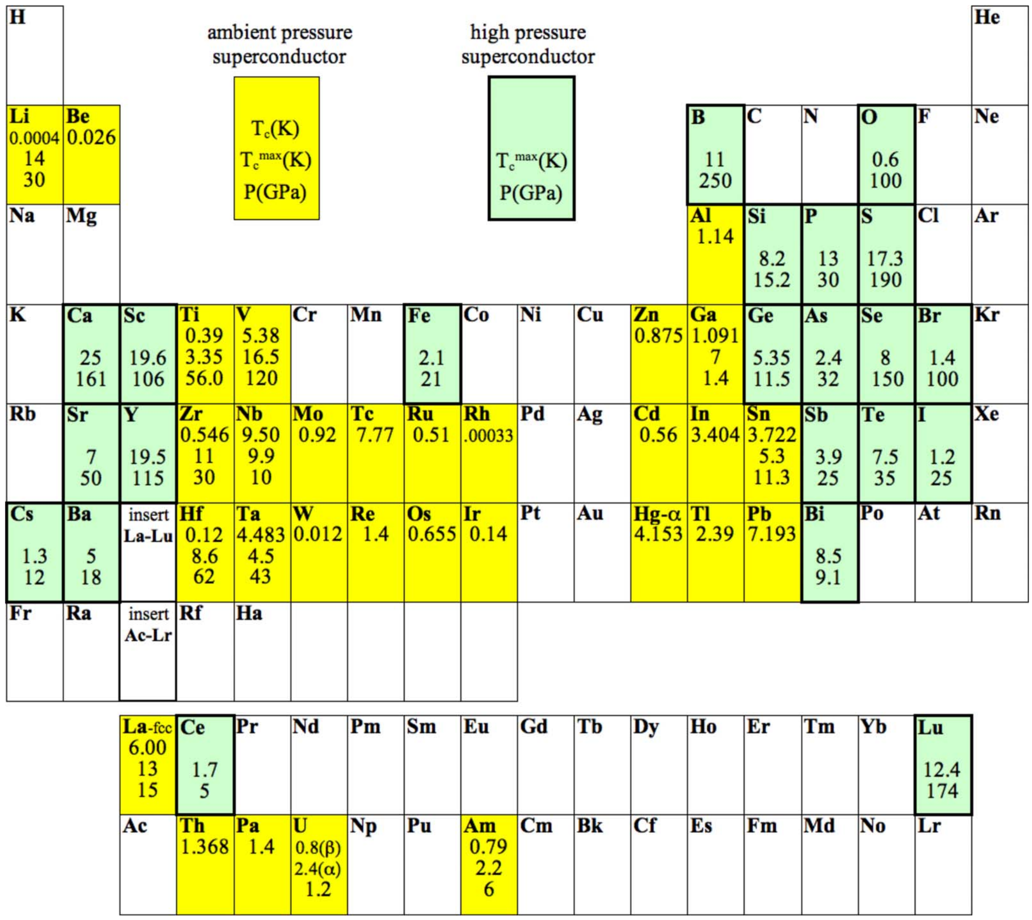

FIG. 1. (Color online) Periodic Table listing 30 elements which superconduct at ambient pressure and 22 elements which only superconduct under high pressure. For each element the upper position gives the value of T_c(K) at ambient pressure; middle position gives maximum value $T_c^{\max}$(K) reached in a high-pressure experiment at P(GPa) (lower position). In many elements multiple phase transitions occur under pressure. If T_c decreases under pressure, only the ambient pressure value of T_c is given. Except for Sc and Lu, sources for T_c values at ambient and high pressure are given in Ref. 2.

nonical electronic density of states dependence.

In this paper we examine whether there is a correlation between the change in T_c under pressure and the d-electron count N_d which increases under pressure as the fractional atomic volume of the ion core increases. As the relative increase in N_d with pressure is particularly large for the "early" transition metals where N_d is small, we focus our attention first on the four trivalent d-electron metals Sc, Y, La, and Lu, of which only La superconducts at ambient pressure. Previous high-pressure studies on Sc,[24] Y,[10] La,[16] and Lu (Ref. 25) were restricted to pressures of 74, 115, 50, and 28 GPa, respectively. Here we present new data which determine $T_c(P)$ for Sc and Lu to the significantly higher pressures of 123 and 174 GPa, respectively. Whereas in Lu T_c increases monotonically with pressure to 12.4 K at 174 GPa, in Sc T_c increases rapidly with pressure, reaching a maximum value of 19.6 K at 107 GPa in the Sc-II phase. If the pressure is increased further, Sc-II transforms to Sc-III (Refs. 26 and 27) whereupon T_c drops to 8.31 K at 111 GPa. Sc possesses with 19.6 K the second highest value of T_c of any elemental superconductor. An interesting correlation is revealed between the value of T_c for these four metals and the increasing fractional ion core volume under pressure.

II. EXPERIMENT

The diamond anvil cell (DAC) used in the present experiment is made of both standard and binary CuBe alloy and utilizes a He-gas-driven double membrane to change the force between the two opposing diamond anvils at any temperature.[28] Temperatures as low as 1.55 K can be reached in an Oxford flow cryostat. The 1/6-carat, type Ia diamond anvils have 0.18 mm culets beveled at 7° out to 0.35 mm with a 3 mm girdle. The metal gasket is a disk made of $W_{0.75}Re_{0.25}$ alloy 3 mm in diameter, 250 μm thick, and preindented to 25–30 μm; a 90 μm diameter hole is electrospark drilled through the center of the gasket. High-purity ingots of Sc and Lu (99.98% metals basis) were obtained from the Materials Preparation Center of the Ames Laboratory.[29] Small chips of Sc or Lu were cut from the ingots and then packed as densely as possible into the gasket hole. Several tiny ruby spheres[30] were placed next to the sample to allow the determination of the pressure *in situ* at 20 K from the R_1 ruby fluorescence line with resolution ±0.2 GPa using the revised pressure scale of Chijioke *et al.*[31] An Ar ion or HeCd laser was used to excite the ruby fluorescence. To maximize the sample diameter under extreme pressure conditions, and thus the magnitude of the diamagnetic signal at the superconducting transition, no pressure medium was used in the present experiments. In previous experiments on Y,[10] no measureable difference was observed in the pressure dependence of T_c with (dense He) or without pressure medium in the 35–90 GPa pressure region where they could be compared. One should not forget, however, that in nonhydrostatic experiments employing no pressure medium, shear stress effects may have a significant influence on how T_c changes under pressure.[2,32,33]

The highest pressure reached in the present experiments was 174 GPa (1.74 Mbar) for Lu. As can be seen in Fig. 2(a), this extreme pressure is sufficient to cause the nominally flat culet surface of the diamond anvils to cup which leads to the black halo around the Lu sample in reflected white-light illumination. At this 174 GPa pressure the ruby line became too weak to be detected. In this case the pressure was determined from the first-order Raman spectrum[34] of the diamond anvil [see Fig. 2(b)] taken from a spherical region ~ 20 μm in diameter centered on the Lu sample [blue region in Fig. 2(a)]. The Raman signal from outside of this region was rejected by the confocal microscope optics.

The superconducting transition is detected inductively using two compensating primary/secondary coil systems [see Fig. 2(c)] connected to a Stanford Research SR830 digital lock-in amplifier via a SR554 transformer preamplifier; the excitation field for the ac susceptibility studies is 3 Oe rms at 1023 Hz. Under these conditions and considering the calibration of the coil system, the anticipated diamagnetic signal in nanovolt for a superconducting transition with 100% shielding is given from Ref. 35 by

$$S(nV) = 8.17 \times 10^{-5}[V \backslash (1 - \mathcal{D})], \qquad (1)$$

where V is the sample volume in $(\mu\text{m})^3$ and $\mathcal{D}$ is the demagnetization factor. Since the sample is a flat cylinder, $V = \pi h d^2/4$, where h and d are the sample thickness and diameter, respectively. In the limit $h/d \ll 1$, Joseph[36] has derived the approximate expression

$$\mathcal{D} \approx 1 - [2h/(\pi d)][\ln(8d/h) - 1]. \qquad (2)$$

In the present experiments to extreme pressure the sample dimensions are typically $d \simeq 80$ μm and $h \simeq 15$ μm, yielding $\mathcal{D} \approx 0.671$ and thus $S \approx 20$ nV. A more accurate calculation[37] finds $\mathcal{D} \approx 0.73$ and thus $S \approx 25$ nV.

To facilitate the identification 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 over the temperature range 5–50 K. This lower limit in the effective temperature range is not dictated by the cryostat, which can cool to 1.55 K, but by the fact that the superconductivity of the W-Re gasket leads to a large diamagnetic signal which swamps the sample signal below ~ 5.2 K, a temperature which has negligible pressure dependence. For this reason the superconducting transition of the sample can only be reliably detected if it occurs at a temperature $T_c \gtrsim 5.5$ K. A relatively low noise level of a few tenths of a nanovolt is achieved by: (a) using the transformer preamplifier to ensure good impedance matching, (b) varying the temperature very slowly (100 mK/min) at low temperatures, (c) using a long time constant (>3 s) on the lock-in amplifier, and (d) averaging over 2–3 measurements. Further experimental details of the high-pressure and ac susceptibility techniques are published elsewhere.[24,28,32]

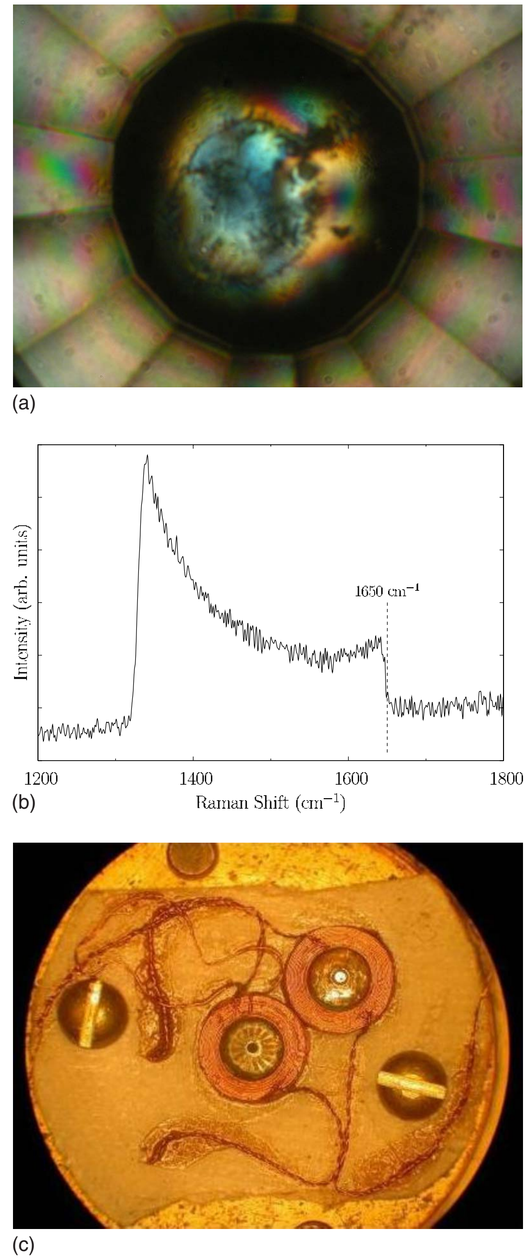

FIG. 2. (Color online) (a) Micrograph in reflected white light of Lu sample in W-Re gasket at 174 GPa; black annular ring signals cupping of the diamond culet (180 μm diameter) at these extreme pressures. (b) Raman spectrum from center of diamond anvil culet. High-energy edge of diamond vibron spectrum at 1650 cm^{-1} corresponds to pressure of 174 GPa (Ref. 34). (c) Two identical compensating primary/secondary coil systems (each 180 turns of 60 μm diameter Cu wire) for ac susceptibility measurements. The active coil is around 16-facet diamond anvil in the middle; compensating coil contains a W-Re dummy gasket.

III. RESULTS OF EXPERIMENT

A. Sc metal

The initial pressurization of the Sc sample was carried out at room temperature. The force between the diamond anvils was gradually increased until the gasket hole completely closed around the sample, compressing it to full density. At this point the pressure on the sample was approximately 20 GPa and the sample diameter had decreased from 90 to 85 μm. Increasing the pressure to 35 GPa resulted in no further decrease in the sample diameter. The height of the hole in the gasket containing the sample varied between the initial preindentation thickness of 26 μm and the final thickness after the experiment 17 μm; we estimate the sample thickness during the high-pressure experiment to be 17–20 μm.

Following the initial pressurization to 35 GPa, the DAC was cooled to low temperatures to search for a superconducting transition. None was observed above 5.5 K in the ac susceptibility at 35, 56, or 66 GPa, whereby the DAC was kept at a temperature below 160 K to expedite the experimentation. After warming the DAC back to ambient temperature, 81 GPa pressure was applied and the DAC cooled down and kept below 160 K for the rest of the experiment. As seen in Fig. 3(a), at 81 GPa a superconducting transition does appear where T_c increases with pressure to a value as high as 19.6 K at 107 GPa, but then drops to a much lower temperature at 123 GPa. The magnitude of the superconducting transition (~20–30 nV), which is consistent with 100% shielding, is much larger than that (~3–4 nV) in the previous nearly hydrostatic experiments on Sc by Hamlin *et al.*[24] to 74.2 GPa. This is due to the larger sample volume and larger demagnetization factor in the present nonhydrostatic experiments. Note that we define T_c as the temperature at the midpoint of the diamagnetic transition.

In Fig. 3(b) the dependence of T_c for Sc on pressure is plotted for all data in the present experiment (unprimed numbers) and compared to the earlier high-pressure studies of Wittig[38] to 21.5 GPa in solid steatite pressure medium (solid line) and those of Hamlin *et al.*[24] to 74.2 GPa in nearly hydrostatic He pressure medium (primed numbers). For all three sets of data using diverse pressure media, the dependence of T_c on pressure appears to follow a reasonably smooth, monotonically increasing curve to 107 GPa. As we also found for Y,[10] therefore, the $T_c(P)$ dependence for Sc does not appear to depend sensitively on the degree of shear stress on the sample. We note, however, that the absence of a superconducting transition above 5.5 K in the present experiment at 66 GPa does appear to conflict with the nearly hydrostatic data point 2′ of Hamlin *et al.*[24] in Fig. 3(b) where $T_c \approx 6.2$ K at 66.8 GPa, thus pointing to possible minor shear stress effects on $T_c(P)$ in the present experiment.

Between 0 and 123 GPa, the highest pressure reached in the present experiments, Sc undergoes two structural phase transitions [see phase boundaries in Fig. 3(b)].[26,27] Whereas no $T_c(P)$ data is available across the I→II boundary, T_c is seen to drop sharply at the II→III boundary and then rise slowly as the pressure is increased further. The value of $T_c \simeq 19.6$ K (susceptibility midpoint) reached at 107 GPa

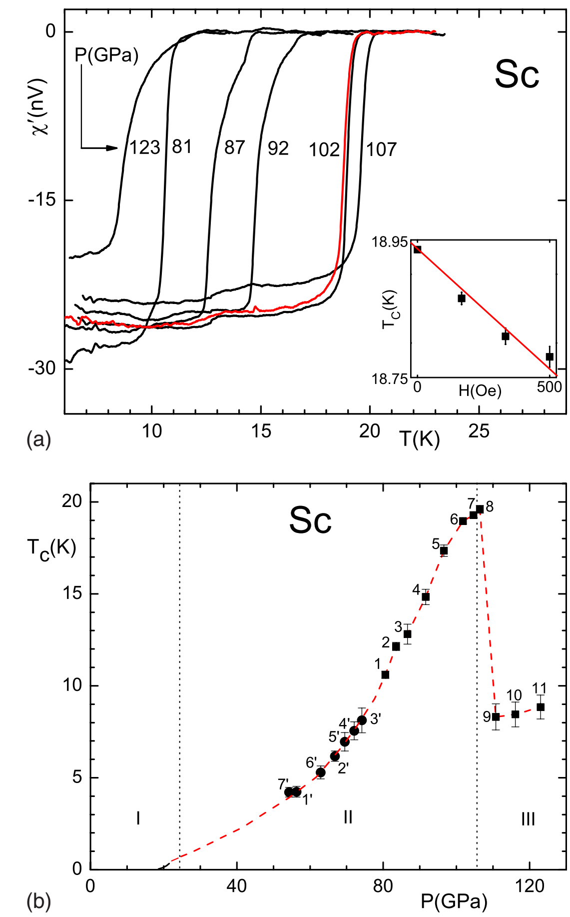

FIG. 3. (Color online) (a) Real part of the ac susceptibility signal in nV versus temperature for Sc at selected pressures to 123 GPa. Pressure was increased monotonically. Applying 500 Oe dc magnetic field shifts superconducting transition at 102 GPa to lower temperatures by 160 mK. Inset: T_c versus magnetic field H at 102 GPa. The vertical bars give error in shift of T_c using the transition for $H=0$ as reference. (b) Superconducting transition temperature versus pressure in present experiment (■, unprimed numbers), from Ref. 24 (●, primed numbers), and from Ref. 38 (short solid line). The "error bars" give 20–80 transition width. The numbers give order of measurements. The dashed line through data is a guide for the eye. The vertical dashed lines mark phase boundaries I→II and II→III.

shortly before the II→III phase transition is the second highest value of T_c ever observed in an elemental superconductor, trailing only Ca with $T_c \approx 25$ K (resistivity onset) at 160 GPa.[9] Note that the highest value reached for Y is $T_c \simeq 19.5$ K (susceptibility midpoint) at 115 GPa.[10] At 48 GPa Li shows a superconducting onset in the electrical resistivity at 20 K, but the transition midpoint lies at least 5 K lower.[11]

As expected for a superconducting transition, T_c decreases in a dc magnetic field. The transition in Fig. 3(a) at 102 GPa was measured after a 500 Oe magnetic field was applied at 25 K (solid red line). The dependence of T_c at this pressure on magnetic field H to 500 Oe is shown in the inset of Fig. 3(a) and is seen to decrease approximately linearly with H at the rate $dT_c/dH \simeq -0.30$ mK/Oe. For the superconducting transitions in Sc at 81, 87, 97, 102, 111, and 123 GPa, where $T_c(H=0) \equiv T_{co} = 10.6$, 12.8, 17.4, 18.9, 8.31, and 8.85 K,

dT_c/dH takes on the values −0.63, −0.56, −0.49, −0.30, −0.78, and −0.78 mK/Oe, respectively. Hamlin *et al.*[24] reported for data point 3′ in Fig. 3(b), where $T_c \approx 8.2$ K, that $|dT_c/dH| \le 0.3$ mK/Oe. For an Y sample with $T_c \simeq 9.7$ K at 46.6 GPa, T_c was found to decrease under magnetic fields to 500 Oe at the rate −0.5 mK/Oe, a comparable value to those found for Sc.[10] An attempt to extend the present experiment on Sc to pressures above 123 GPa resulted in the destruction of one of the two diamond anvils, thus ending the experiment.

B. Lu metal

A single high-pressure ac susceptibility experiment was carried out on pure Lu metal. The $W_{0.75}Re_{0.25}$ gasket was preindented to 29 μm and, as for Sc, the Lu sample was loaded into the 90 μm diameter gasket hole. The DAC was then pressurized at ambient temperature to ∼20 GPa whereupon the diameter of the bore containing the sample decreased from 90 to 83 μm. The DAC was then cooled to low temperatures to search for a superconducting transition in the temperature range above 5.5 K, a limit dictated, as before with Sc, by the superconducting transition of the W-Re gasket below 5.2 K. No superconducting transition was detected above 5.5 K at pressures of 40, 62, and 69 GPa. Finally, at 88 GPa a strong diamagnetic transition was observed near 7 K, as seen in Fig. 4(a). Inserting the observed sample diameter of ∼80 μm and estimated 15 μm thickness into Eq. (1), a value for the diamagnetic signal $S \approx 20$ nV is obtained. Since the measured transitions in Fig. 4(a) lie near 30 nV, the indicated diamagnetic shielding is at or near 100%. Given the tiny sample size, the quality of the data is quite remarkable.

T_c for Lu was found to increase monotonically with pressure to 140 GPa, at which point the He-gas pressure P_{mem} in the double membrane reached 45 bars. At higher pressures we could no longer detect the ruby R_1 line. The superconducting transition of Lu was measured to higher pressures by increasing P_{mem} from 45 to 80 bars. For $P_{mem} \le 45$ bars, the dependence of the sample pressure (from the ruby R_1 line) on P_{mem} is well described by a simple linear fit, making a linear extrapolation of this curve to higher pressures seem reasonable. Such an extrapolation yields an estimated sample pressure of 220 GPa for $P_{mem} \approx 80$ bar. To check the validity of this extrapolation, we measured the diamond vibron in the Raman scattering [Fig. 2(b)] at the maximum pressure, as described above, which yielded "only" 174 GPa. The simple extrapolation from $P_{mem} \approx 45$ to 80 bar thus overestimated the sample pressure in the cell by more than 40 GPa. This reduction in the actual pressure likely arises at least in part from progressive "cupping" of the diamond anvil culet surface at extreme pressures, as evidenced by the black annular region clearly visible in Fig. 2(a).

In Fig. 4(b) T_c for Lu is plotted versus pressure for all data in the present experiment. Four of the transitions (points 6–9) occur between 140 and 174 GPa where we made no direct measurement of the pressure. For these points (open circles) we estimate the sample pressure from P_{mem} using a linear interpolation between 140 GPa at 45 bars and 174 GPa at 80 bars. That the dependence of T_c on pressure for Lu is reversible is evidenced by the fact that data point 11, obtained by releasing the pressure from 174 to 120 GPa, lies along the $T_c(P)$ curve for increasing pressure.

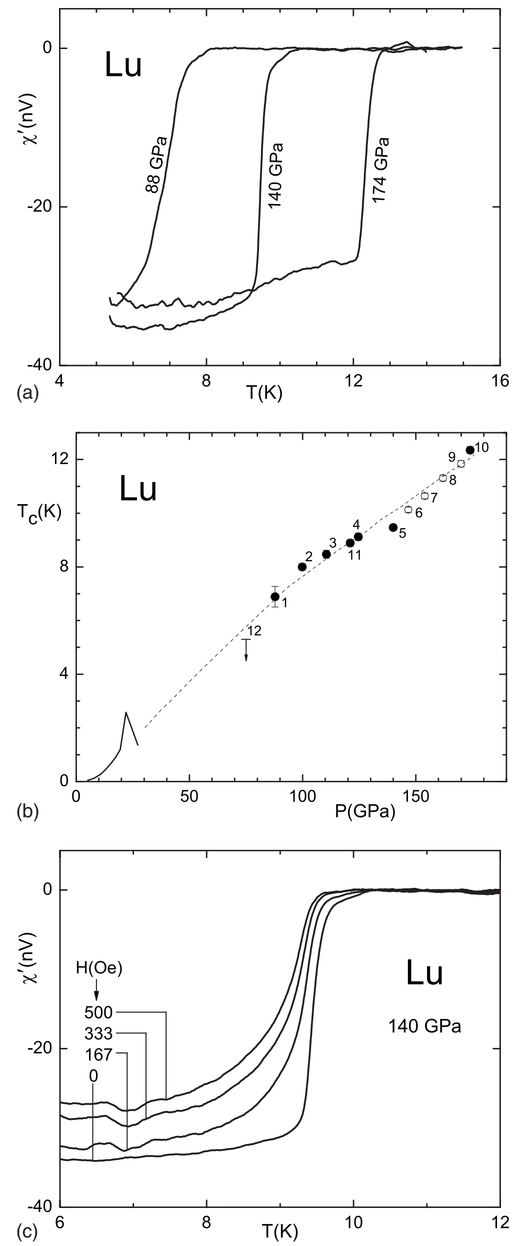

FIG. 4. (a) Real part of the ac susceptibility signal in nV versus temperature for Lu at 88, 140, and 174 GPa pressure. (b) Dependence of T_c on pressure for all data. The "error bars" give 20–80 transition width. The numbers give order of measurement. The dashed line through data is a guide for the eye. At 75 GPa (point 12) no superconducting onset was observed above 5.2 K. The filled circles (●) indicate pressure measured from ruby R_1 line; open circles (○) indicate pressure estimated from double-membrane pressure (see text). (c) Real part of the ac susceptibility signal versus temperature at 140 GPa for dc magnetic fields 0, 167, 333, and 500 Oe.

Lu has been found to transform at room temperature from a double hcp (dhcp) to hR24 structure near 88 GPa and remain in this structure up to at least 163 GPa.[39] Unfortunately, our data do not extend to low enough pressure to allow us to comment on the possible effect of this structural transition on $T_c(P)$. In this experiment there was no catastrophic failure of the diamond anvils upon complete release of pressure. One of the two anvils did show a ring-crack pattern typical for beveled anvil experiments in this pressure range.[40]

The dependence of T_c on dc magnetic fields H up to 500 Oe was measured at most of the pressures. In Fig. 4(c) we show superconducting transitions for Lu measured at 140 GPa and fields of 0, 167, 333, and 500 Oe. The transition temperature decreases monotonically and reversibly with H, as expected for a superconductor. No difference in behavior was observed whether the dc field was applied above or below T_c. The initial slope $dT_c/dH \approx -0.6$ mK/Oe remains constant over the entire pressure range studied. Unlike Sc, the magnitude of the diamagnetic transition for Lu is seen to become noticeably smaller with increasing field. This likely arises since the applied field, which is enhanced by the factor $(1-\mathcal{D})^{-1}$ at the outer perimeter of the pancake-shaped sample, is sufficiently strong for $T<T_c$ to exceed the critical field and penetrate into the outer perimeter of the sample, thus reducing the effective sample diameter d and sample volume V. In fact, from the relative change in the magnitude of the superconducting transition in the applied magnetic field seen in Fig. 4(c), one can estimate[41] the critical field at 0 K and 140 GPa for Lu to be $H_c(0\ K) \approx 1440$ Oe.

In contrast, as seen in Fig. 3(a) for Sc at 102 GPa, there is no measurable decrease in the magnitude of S in 500 Oe magnetic field. The enhanced magnetic field is thus too small to penetrate into the perimeter of the disk-shaped sample. We can, therefore, only put a lower limit on the size of the critical field $H_c(0\ \mathrm{K}) \gtrsim H_o(1-\mathcal{D})^{-1}$. Since from Eq. (2) for $h \simeq 17$ μm and $d \simeq 85$ μm (see above) it follows that $\mathcal{D} \simeq 0.658$, for Sc at 102 GPa we estimate that $H_c(0\ \mathrm{K}) \gtrsim (500\ \mathrm{Oe})(1-0.658)^{-1} = 1460$ Oe.

IV. DISCUSSION

A. Phenomenological model

In Fig. 5(a) we directly compare the pressure dependences of T_c for Sc and Lu with the results of previous studies on the other trivalent d-electron metals Y (Refs. 10 and 42) and La.[16] $T_c(P)$ for Y and La appears to pass through a maximum value at ~120 and 12 GPa, respectively, however, $T_c(P)$ for La displays considerably more structure over its pressure range to 50 GPa than for the other three to over 100 GPa. This may be at least partly a result of the relatively high compressibility of La metal. In Fig. 5(b) we utilize the measured equations of state of Sc,[26] Y,[43] La,[43] and Lu (Ref. 39) to convert the data in Fig. 5(a) to plots of T_c versus relative volume V/V_o, where V_o is the sample volume at ambient pressure.[44] Note that for Sc, Y, and Lu the dependence of T_c on V/V_o exhibits a positive curvature over an appreciable region.

We first attempt a simple phenomenological analysis of the volume dependences of T_c in Fig. 5(b) using the McMillan equation

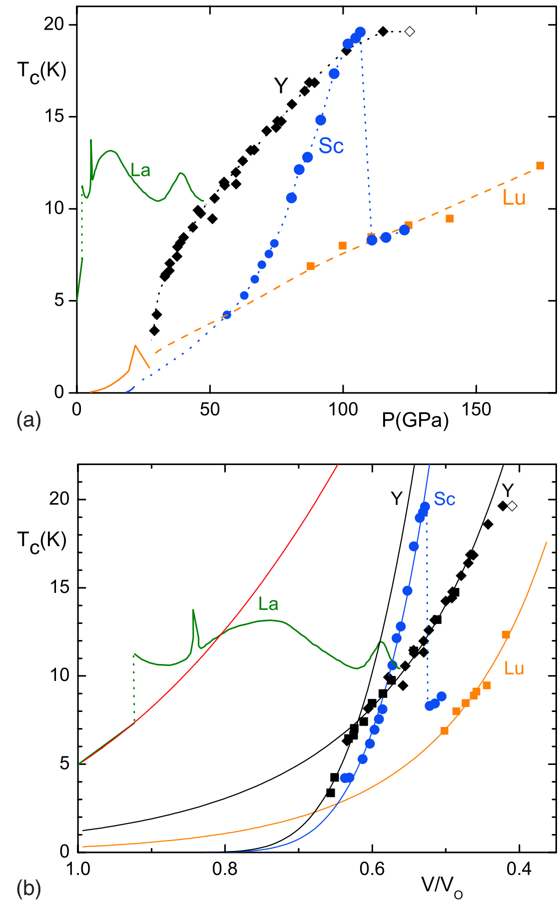

FIG. 5. (Color online) (a) T_c versus pressure for the trivalent d-electron metals Sc (●), Y (◆), La (solid line), and Lu (■). The dashed lines are guides for the eye. The pressure for the open diamond (◇) data point for Y is extrapolated (Ref. 42). (b) T_c versus relative volume using the $T_c(P)$ data from Fig. 5(a). The solid lines are fits to the data using the McMillan equation (see text). For La only the data for $V/V_o > 0.92$ are fit.

$$T_c \simeq \frac{\langle\omega\rangle}{1.20}\exp\left[\frac{-1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right], \tag{3}$$

where $\lambda \equiv \eta/(M\langle\omega^2\rangle)$ is the electron-phonon coupling parameter, η the Hopfield parameter, ω a phonon frequency, μ^* the Coulomb repulsion, and M the ionic mass.[23] If we define $\gamma \equiv -\partial \ln\langle\omega\rangle/\partial \ln V$ and $\varphi \equiv \partial \ln \lambda/\partial \ln V$, assume γ and φ are independent of pressure, and integrate, we obtain

$$\langle\omega\rangle_V = \langle\omega\rangle_o[V/V_o]^{-\gamma} \text{ and } \lambda(V) = \lambda(V_o)[V/V_o]^{\varphi}, \tag{4}$$

where $\varphi \simeq \partial \ln \eta/\partial \ln V + 2\gamma$. 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.[2] Since 2γ is positive, whether λ (and T_c) increases or decreases with pressure depends on whether $|d \ln \eta/d \ln V| > 2\gamma$ or vice versa. The next step is to fix the values of $\langle\omega\rangle_o$ and γ from experimental data,[45] set $\mu^*=0.1$, and then find the best fit to the dependence of T_c on relative volume in Fig. 5(b) by using $\lambda(V_o)$ and $\partial \ln \eta/\partial \ln V$ as fit parameters.[35] Since at ambient pressure dhcp La superconducts with $T_c(V_o) \simeq 5$ K,[16] Eq. (3) is used to determine $\lambda(V_o)$ for La.

As seen in Fig. 5(b), the fits obtained using Eq. (3) are reasonably successful. For Y there is a clear change in slope near $V/V_o \approx 0.63$ where a structural phase transition occurs (Sm-type →dhcp)[43,46] so that two fits are carried out, one for the "low-T_c" and the other for the "high-T_c" values. The values of the two fit parameters used $(\lambda(V_o), \partial \ln \eta / \partial \ln V)$ are found to be (0.166, −4.15), (0.127, −5.50) (0.459, −2.83), (0.844, −4.03), and (0.366, −2.81) for Sc, Y(low-T_c), Y(high-T_c), La, and Lu, respectively, allowing the estimate that at ambient pressure T_c equals 0 K, 0 K, 1.2 K, 5.0 K, and 0.31 K. From experiment it is known that $T_c(V_o) < 6$ mK for Y,[25] <30 mK for Sc,[47] and <22 mK for Lu[48] which agrees reasonably well with the estimates above. Note that from the Y(high-T_c) fit $T_c(V_o) \approx 1.2$ K is predicted, meaning that if Y would remain metastable in its dhcp phase at ambient pressure, it should superconduct at $T_c \approx 1.2$ K, a value more than 2 orders of magnitude higher than that (<6 mK) in its thermodynamically stable hcp structure. Extrapolating the fit curves in Fig. 5(b) to higher pressures leads to the estimate that, barring structural transitions, T_c would reach 30 K at 127, 164, 53, and 580 GPa for Sc, Y(high-T_c), La, and Lu, respectively.

B. Electronic structure calculations

The above phenomenological analysis shows that the $T_c(P)$ dependences observed for Sc, Y, La, and Lu appear consistent with moderately strong-coupled, phonon-mediated superconductivity using reasonable values of the averaged parameters. However, to pinpoint the mechanism(s) responsible for the significant increase in T_c with pressure in experiment, detailed electronic structure calculations are needed. Nixon *et al.*[49] recently used an augmented plane-wave (APW) method to calculate the electronic structure of Sc assuming, for simplicity, an fcc phase. Over the pressure range 20 to 80 GPa they find that the Hopfield parameter η increases by nearly a factor of 4, whereas the electronic density of states $N(E_f)$ decreases by 15%, the Coulomb repulsion μ^* decreasing by only 5%. Using the McMillan formula in Eq. (3), they find that over the given pressure range to 80 GPa T_c increases from 0.4 to 7 K, in reasonable agreement with experiment.

The same group[50] used similar techniques to estimate the electronic structure of fcc Y to pressures somewhat above 1 Mbar (113 GPa). They estimate that over the pressure range 40–113 GPa T_c increases by 5–10 K, depending on the value chosen for μ^*, the best agreement occurring for $\mu^*=0.04$. Linear response methods were applied by Yin *et al.*[51] who included pressure-dependent changes in the lattice vibration spectrum of fcc Y metal in their calculation. They conclude that the large positive value of dT_c/dP arises from a pressure-induced softening in the transverse phonon modes, i.e., a negative mode Grüneisen parameter, in contrast to the positive value $\gamma \simeq 1.08$ used in the above phenomenological analysis. Singh[52] has recently applied density-functional theory to both hcp and dhcp Y metal to calculate the changes under pressure of both the electronic properties and the lattice vibration spectrum. A substantial increase in the electron-phonon coupling with pressure is found yielding a value of T_c for dhcp Y as high as 19 K.

Some time ago Pickett *et al.*[53] carried out a linearized APW calculation for fcc La to 12 GPa. They find that, as with Sc and Y, the strong increase in T_c with pressure arises primarily from a significant enhancement of the Hopfield parameter η. In their DAC studies on La to 50 GPa, Tissen *et al.*[16] suggest that the abrupt increase in T_c near 2 GPa likely arises from the dhcp→fcc structural phase transition, whereas some of the marked features in $T_c(P)$ at higher pressures may arise because of $s \rightarrow d$ transfer which pushes the Fermi energy up through van Hove singularities.

In 1990 Skriver and Mertig[54] calculated the strength of the electron-phonon coupling parameter λ at ambient pressure, obtaining for Sc, Y, La, and Lu the values 0.57, 0.53, 0.90, and 0.59, respectively. Note that the only ambient-pressure superconductor in the group, La, has a much higher calculated value of λ than the other three.

It would be useful if a single state-of-the-art electronic structure calculation of the properties relevant for superconductivity would be carried out for Sc, Y, La, and Lu to pressures into the Mbar region. Because of the close electronic similarity of these four systems, much could be learned about the efficacy of this type of calculation for predicting superconducting properties in general.

C. *d*-band occupancy

As mentioned in Sec. I, the equilibrium crystal structure under ambient conditions across the 3*d*, 4*d*, and 5*d* transition metal series, as well as across the rare-earth series from La to Lu, has been shown to be closely related to the occupancy of the *d*-band N_d. We now explore the question whether in *d*-electron metals the superconducting transition temperature T_c might itself be correlated with N_d, restricting ourselves here to the four electronically closely related trivalent *d*-electron metals Sc, Y, La, and Lu.

The *d*-electron count N_d increases under pressure due to $s \rightarrow d$ transfer which is driven by the increase in the fractional ion core volume V_c/V_a,[21,55] where we define the ion core volume $V_c \equiv (4/3)\pi R_c^3$ and the atomic volume $V_a \equiv (4/3)\pi R_{WS}^3$ (R_{WS} is the Wigner-Seitz radius), yielding $R_{WS}/R_c = (V_a/V_c)^{1/3}$. The conduction electrons must stay out of the ion core volume V_c and thus are confined to the free sample volume $V_f \equiv V_a - V_c$ outside the ion cores. Under pressure the atomic volume V_a decreases whereas V_c remains nearly constant. The ratio R_{WS}/R_c, therefore, is a measure of how much free volume remains for the conduction electrons under pressure. The ratio R_{WS}/R_c decreases under pressure; the closer it approaches the minimum possible value 1, the less free volume is available and the greater the anticipated degree of *s*-*d* transfer.[21,55]

Many years ago Johansson and Rosengren[19] showed that the T_c values for Y, La, Lu, and alloys thereof are a smooth function of a similar ratio[56] which decreases under pressure, as does T_c. We pursue a similar analysis here where R_{WS} at ambient pressure is calculated from the molar volume and R_c is obtained from the trivalent ionic radii for coordination number 6.[57] We assume that R_c is independent of pressure so that applying high pressure monotonically *decreases* the value of the ratio R_{WS}/R_c. To determine how R_{WS}/R_c

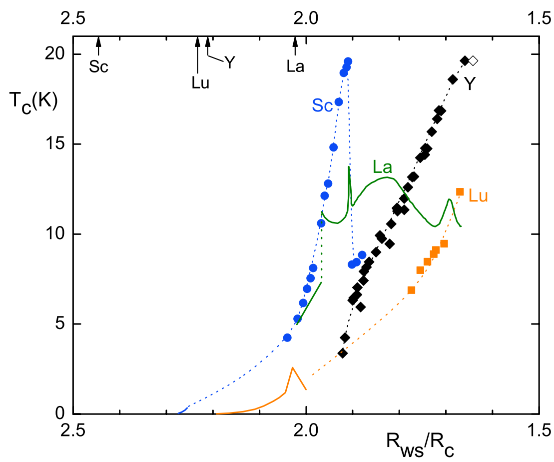

FIG. 6. (Color online) T_c versus ratio of Wigner-Seitz radius to core-electron radius R_{WS}/R_c for Sc, Y, La, and Lu. The dashed lines are guides for the eye. The vertical arrows at the upper axis show ambient pressure values of R_{WS}/R_c for the indicated elements.

changes at high pressure, we simply multiply it by $(V/V_o)^{1/3}$, where V/V_o is given by the equations of state for Sc, Y, La, and Lu cited above.

In Fig. 6 we plot T_c versus R_{WS}/R_c for Sc, Y, La, and Lu. One sees immediately that the data for these four metals are more tightly grouped together than in the previous figures where T_c was plotted versus pressure P or relative volume V/V_o. The ratio R_{WS}/R_c, therefore, appears to be a more relevant parameter to describe the superconducting properties than P or V/V_o. Some simple systematics are evident in Fig. 6. Initially, at least, T_c generally increases with pressure. Interestingly, the T_c values of all four elements do not exceed 1 K until the ratio R_{WS}/R_c is reduced to a value below ~2.1. This clarifies why La is the only member in this group that is superconducting at ambient pressure; for La at ambient pressure R_{WS}/R_c=2.02, whereas for the other three metals R_{WS}/R_c>2.1 (see vertical arrows below upper axis in Fig. 6).

Under pressure the d-electron count N_d for Sc, Y, La, and Lu increases.[21,55,58] Duthie and Pettifor[21] and Pettifor[55] have shown that the occupation of the d band is closely related to the fractional volume of the ion core with smaller relative volumes leading to greater occupation of the d band. The effect of compression on the d-band occupancy has been recently calculated for Sc, Y, La, and Lu by Yin and Pickett[58] and is shown in Fig. 7(a) where N_d is plotted versus V/V_o. Note that N_d increases monotonically with pressure (decreasing V/V_o), being largest for La metal over almost the entire range. Figure 7(b) shows that for Sc, Y, and La the ratio R_{WS}/R_c has nearly a one-to-one correspondence with the calculated d-electron count N_d, the dependence for Lu being shifted toward lesser N_d values.

In Fig. 8 the data in Figs. 5(b) and 7(a) are used to plot T_c versus N_d for all four metals. Compared to the data in Fig. 6, where T_c is plotted versus the ratio R_{WS}/R_c, the curves for Y, La, and Lu do appear to be grouped closer together, but that for Sc has moved somewhat further away. It is thus not clear whether the ratio R_{WS}/R_c or the d-electron count N_d is the superior parameter for describing changes in the superconducting properties under pressure.

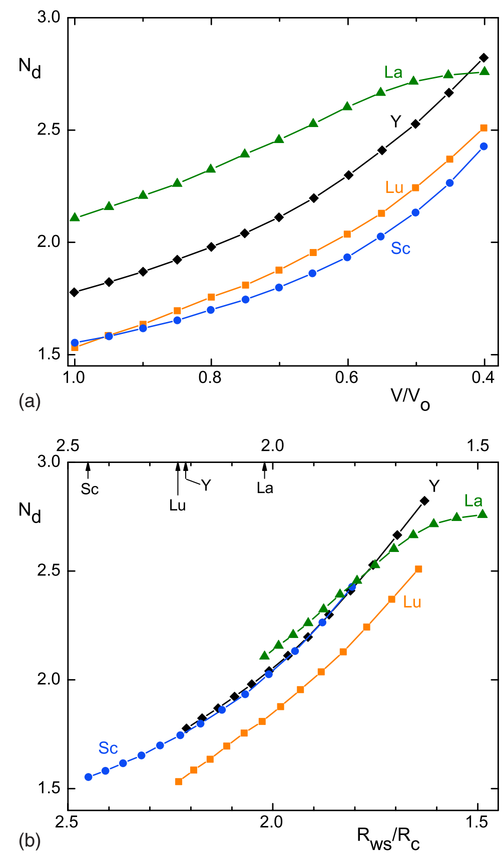

FIG. 7. (Color online) (a) Calculated occupation of d-band N_d versus relative volume V/V_o for Sc, Y, La, and Lu from Yin and Pickett (Ref. 58). (b) N_d versus the ratio R_{WS}/R_c from the data in (a). The solid lines connect calculated data points.

Since T_c generally increases with N_d, one expects that when the d occupation reaches its maximum value N_d=3, the pressure dependence of T_c should change, perhaps passing through a maximum. According to Fig. 7(b), however, the principal maximum in $T_c(P)$ for La occurs at a value N_d ≈2.4 which is well below N_d=3. Sc, being the least com-

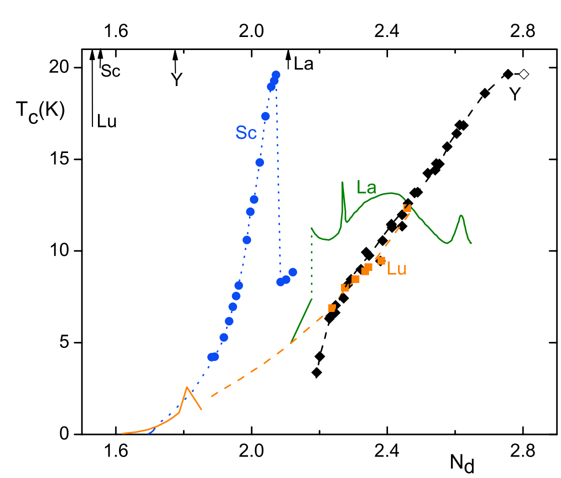

FIG. 8. (Color online) T_c versus N_d using data from Figs. 5(b) and 7(a). The vertical arrows at the upper axis show ambient pressure values of N_d for the indicated elements.

pressible and having the largest ambient pressure value of R_{WS}/R_c, is the furthest from completion of s-d transfer in the present experiment. Indeed, the data for Sc in Fig. 7(b) would imply that it would take a pressure much higher than 2 Mbar before s-d transfer is completed. This suggests that, had the structural phase transition in Sc at 110 GPa not occurred, T_c might have reached values near 30 K according to an estimate using the phenomenological model above.

The Sc-II phase, in which Sc exhibits its highest value $T_c \simeq 19.6$ K, the second highest behind Ca (Ref. 9) for any elemental superconductor, is an unusual incommensurate host-guest crystal structure.[26] This type of crystal structure was only recently found to exist in high-pressure phases of elemental solids.[59] It would be very interesting to study these metals to much higher pressures in order to investigate to what heights T_c for Sc and Lu will increase. In view of its light molecular weight and exceptionally high value of T_c, ultra-high-pressure experiments on Sc are particularly promising. In addition, Sc undergoes a further structural transition to Sc-IV at 130 GPa (Ref. 26) which may well leave its mark on the superconducting properties.

In summary, the dependence of the superconducting transition temperature of Sc and Lu on pressure has been determined to pressures well above 1 Mbar whereby T_c for Sc reaches a value as high as 19.6 K, the second highest transition temperature ever observed for an elemental superconductor. Comparing $T_c(P)$ for the closely related trivalent metals Sc, Y, La, and Lu reveals that the observed rapid increase in T_c under pressure is correlated with a strong increase in the concentration of d-electrons in the conduction band. In these conventional electron-phonon superconductors, particulary in Sc, there is the possibility that T_c may reach values exceeding 30 K at even higher pressures.

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[42] The data point (◇) for Y at 125 GPa in Fig. 5(a) was added to the published data (◆) to 115 GPa from Ref. 10. At this highest pressure the ruby manometer failed (intensity too low); the sample pressure of 125 GPa was estimated by extrapolation from the He-gas pressure P_{mem} in the double membrane, where P_{mem} is proportional to the force pushing the diamond anvils together.
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