

# Superconducting Phase Diagram of Li Metal in Nearly Hydrostatic Pressures up to 67 GPa

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The dependence of the superconducting transition temperature  $T_c$  on nearly hydrostatic pressure has been determined to 67 GPa in an ac susceptibility measurement for a Li sample embedded in helium pressure medium. With increasing pressure, superconductivity appears at 5.47 K for 20.3 GPa,  $T_c$  rising rapidly to  $\sim 14$  K at 30 GPa. The  $T_c(P)$  dependence to 67 GPa differs significantly from that observed in previous studies where no pressure medium was used. Evidence is given that superconductivity in Li competes with symmetry breaking structural phase transitions which occur near 20, 30, and 62 GPa. In the pressure range 20–30 GPa,  $T_c$  is found to decrease rapidly in a dc magnetic field, the first evidence that Li is a type I superconductor.

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Of the 52 elemental solids known to be superconducting, 23 enter this state only if compressed under sufficiently high pressures [1]. The latest confirmed member of this ever growing family is the alkali metal Li, an element devoid of superconductivity at ambient pressure to temperatures as low as 4 mK [2]. Following an early report of possible pressure-induced superconductivity in Li near 7 K [3], recent electrical resistivity studies by Shimizu *et al.* [4] to 48 GPa (480 kbar) followed by ac susceptibility and resistivity studies by Struzhkin *et al.* [5] to 80 GPa confirmed the onset of a superconducting state for pressures above 20 GPa. The observed dependences of  $T_c$  on pressure in these three experiments, however, are in poor agreement. This may result from the fact that no pressure medium was used, the ultrahard diamond anvils [4,5] or boron-nitride spacers [3] pressing directly onto the Li sample, subjecting it to shear stress and plastic flow. Shear-stress effects on  $T_c(P)$  are well known from studies on such diverse superconducting materials as organic metals [6], high- $T_c$  oxides [7], MgB<sub>2</sub> [8], and Re metal [9];  $\beta$ -Hg, a shear-stress-induced body-centered tetragonal modification of ordinary rhombohedral  $\alpha$ -Hg, exhibits distinctly different superconducting properties [10]. In a substance like Li, where a multitude of potential phases lie very close in energy [11,12], the shear stress may be sufficient to induce structural phase transitions.

Shimizu *et al.* [4] reported that  $T_c$  decreases only slightly in moderate magnetic fields, a field of 30 000 Oe being required to completely suppress Li's superconductivity at 34 GPa. This would indicate that Li is a type II superconductor, an unexpected result for an elemental superconductor, particularly for a simple (*s,p*-electron) metal, like Li.

Neaton and Ashcroft [11] have obtained the counterintuitive result that under sufficient compression the electronic structure of fcc Li departs radically from free-electron-like behavior. The anomalous increase in the magnitude of the pseudopotential (and the electron-

ion interaction) in the fcc phase under pressure leads not only to the possibility of a superconducting state in Li, one where  $T_c$  might increase significantly with pressure, but also to possible structural transitions to phases with reduced symmetry, such as a Li-ion pairing phase [11] or the reduced-symmetry *hR1* or *cI16* phases observed by Hanfland *et al.* [12] for Li near 180 K. In Li, therefore, superconductivity and symmetry breaking phase transitions are expected to compete with each other [11] and possibly lead to an anomalous variation in  $T_c$  with pressure. Other superconducting properties, such as whether type I or type II, values of the critical field(s), gap size, etc., may also be anomalous and should be determined.

*Ab initio* electronic structure calculations by Christensen and Novikov [13] predict that under compression fcc Li should exhibit superconductivity where  $T_c$  increases rapidly with pressure, reaching values as high as 50–70 K. An increase in  $T_c$  under pressure is highly anomalous for a simple (*s,p*-electron) metal, like Li. For all known ambient-pressure simple-metal superconductors,  $T_c$  is found to *decrease* under pressure because lattice stiffening effects normally dominate over electronic effects [7]. The accurate determination for Li of the intrinsic dependence of  $T_c$  on pressure is, therefore, of considerable importance.

In this Letter we present an extensive determination of the superconducting phase diagram,  $T_c(P)$ , to 67 GPa for a Li sample surrounded by helium, the most hydrostatic pressure medium known.  $T_c$  is derived from the magnetic signature in the ac susceptibility at 1000 Hz and 3 Oe rms. Over the pressure range to 67 GPa, the pressure dependence  $T_c(P)$  differs significantly from the results of earlier studies where no pressure medium was used [3–5]. After the onset of superconductivity at 5.47 K for 20.3 GPa,  $T_c$  rises rapidly to  $\sim 14$  K at 30 GPa, followed by an abrupt change in the sign of  $dT_c/dP$ , signaling a likely phase transition from fcc to a lower symmetry structure. This transition at 30 GPa appears to illustrate the competition between the superconducting state and

symmetry breaking phase transitions suggested above. In addition,  $T_c$  is found to decrease rapidly with applied dc magnetic field, giving the first evidence that Li is a type I superconductor.

Because Li reacts readily with oxygen, water vapor, and nitrogen, all steps of the sample preparation and pressure cell loading were carried out in an Ar-gas glove box with continuous purification. High pressures were generated using a diamond-anvil cell (DAC) made from nonmagnetic CuBe. Further experimental details of the DAC and ac susceptibility measurement have been reported previously [8].

In the present experiment the miniature Li samples were cut from foil (Alfa Aesar 99.9%) and placed in a  $250\ \mu\text{m}$  diameter hole drilled through the center of a preindented rhenium gasket (see Fig. 1). Tiny ruby spheres allow the determination [14] of the pressure *in situ* to  $\pm 0.2\ \text{GPa}$  at 20 K. Before sealing the gasket hole shut with the opposing diamond anvils, the hole is flooded with liquid helium which acts as pressure medium. The pressure was changed at temperatures in the range 150–180 K; the Li sample was kept at temperatures below 180 K during the entire high-pressure experiment. After the conclusion of the experiment, the Li sample and rhenium gasket were carefully examined. The preindented gasket

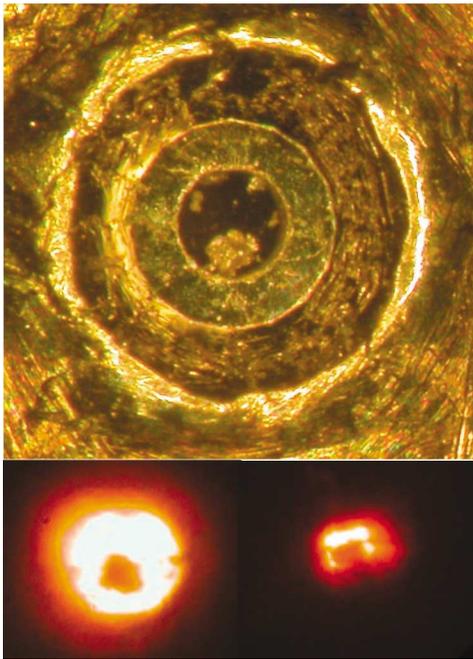


FIG. 1 (color). Top: Reflected-light photograph into Ar-gas glove box of Au-plated rhenium gasket preindented with diamond anvil (0.5 mm diameter culet). In  $250\ \mu\text{m}$  diameter hole are seen for run 2 at ambient pressure the Li sample at 6 o'clock plus clusters of ruby spheres. Bottom: Transmitted-light photograph of hole containing Li sample at (left) ambient pressure and (right) 30 GPa. All three photographs are to the same relative scale.

thickness was found to be reduced from the original 70 to  $35\ \mu\text{m}$  which is still greater than that of the Li sample ( $20\text{--}25\ \mu\text{m}$ ). That neither the diamond anvils nor the gasket wall pressed directly onto the Li sample can be seen in Fig. 1 (bottom right) and can also be inferred from the irregular surface and unaltered shape of the sample after the experiment.

In the present experiment, no superconducting transition was observed for Li in the measured temperature region 4–60 K for applied pressures of 2, 11.5, 19.2, and 19.7 GPa. However, as seen in Fig. 2, at a pressure of 20.3 GPa a clear superconducting transition appears at 5.47 K which increases rapidly with pressure to  $\sim 14\ \text{K}$  at 30.2 GPa before falling and rising again above 50 GPa. The magnitude of the transition is consistent with 100% shielding. In Fig. 3 we summarize the results of our two extensive experiments determining the superconducting phase diagram of Li metal. In the first experiment (run 1) the pressure was first increased in 17 steps to 67 GPa (solid circles) and then decreased in 13 steps to ambient pressure (open circles), both in monotonic fashion. In run 2 (solid triangles) the pressure was increased in eight steps monotonically to 36.5 GPa; a blockage in the cooling line prevented further experimentation. The reproducibility of the data for runs 1 and 2 is seen to be excellent; the  $T_c(P)$  dependence for increasing or decreasing pressure shows only a small pressure hysteresis.

We now discuss in more detail the salient features exhibited by the superconducting phase diagram in

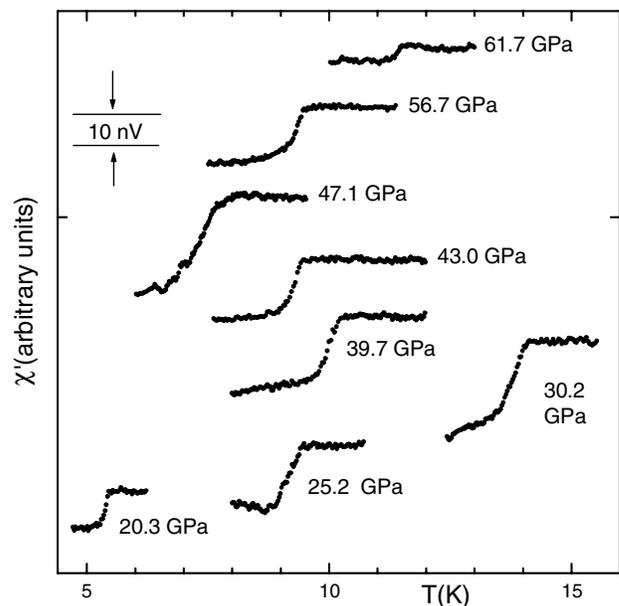


FIG. 2. Superconducting transition of Li in the real part of the ac susceptibility (1000 Hz, 3 Oe rms) for eight values of the pressure. All data are to the same scale but are shifted vertically for clarity. All data are from run 1 for increasing pressure, except data at 20.3 GPa (run 2) and 43.0 GPa (run 1, decreasing pressure).

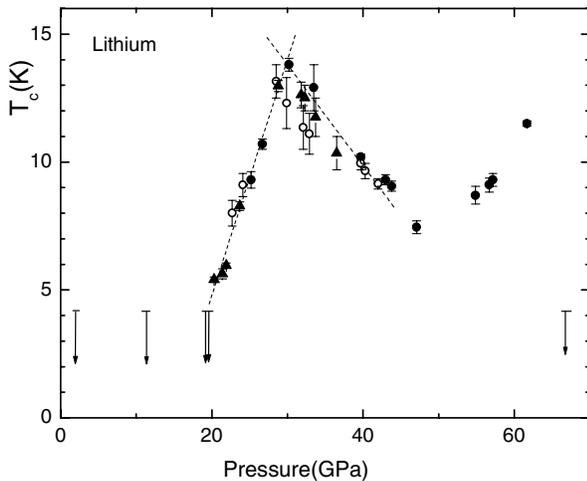


FIG. 3. Superconducting phase diagram of Li metal under nearly hydrostatic pressure: run 1 increasing pressure ( $\bullet$ ), run 1 decreasing pressure ( $\circ$ ), run 2 increasing pressure ( $\blacktriangle$ ). The error in pressure is  $\pm 0.2$  GPa.  $T_c$  is determined by superconducting midpoint to  $\pm 50$  mK; vertical “error bars” give temperatures of the superconducting onset and completion. No superconducting transition is observed above 4 K for pressures below 20 or at 67 GPa. The dashed lines are guides to the eye with slopes  $dT_c/dP \approx +0.9$  K/GPa (left) and  $-0.4$  K/GPa (right).

Fig. 3. The sudden appearance of superconductivity in Li at 5.47 K for 20.3 GPa is likely due to a transition from the low-temperature *Rh6* phase to the fcc structure, as suggested previously [3–5]. Increasing the pressure above 20 GPa,  $T_c$  is seen to rise rapidly at the rate  $dT_c/dP \approx +0.9$  K/GPa, comparable to previous findings [5], to a value near 14 K at 30 GPa. Above this critical pressure the derivative abruptly changes sign to  $dT_c/dP \approx -0.4$  K/GPa, giving clear evidence for a second pressure-induced structural phase transition at 30 GPa. This conclusion is reinforced by the reversible broadening of the superconducting transition in the region 30–36 GPa. In view of the diffraction results on Li at 180 K by Hanfland *et al.* [12], we tentatively identify this second transition as fcc to *cI16*, although a transition from fcc to another phase, such as the intermediate *hR1* phase, is certainly possible. The data near 50 GPa is not sufficiently dense to allow one to speculate whether the minimum in  $T_c(P)$  near this pressure is characteristic for a single phase or arises from a structural phase transition. The abrupt disappearance of superconductivity above 62 GPa, however, signals a further phase transition, perhaps from *cI16* to some unknown phase. Diffraction experiments on Li at temperatures below 50 K under nearly hydrostatic pressure conditions are clearly needed to arrive at an unequivocal structure assignment in the low-temperature region.

Whatever the exact nature of the structural phase transitions indicated by the data in Fig. 3 for pressures

above 20 GPa, it is almost certain that they are from the high symmetry fcc structure to phases of lower symmetry, such as *cI16* or *hR1*. The highly anomalous increase in  $T_c$  with pressure between 20 and 30 GPa in the fcc phase agrees with the trend indicated in the calculation of Christensen and Novikov [13] and bears witness to the large enhancement in the pseudopotential and the electron-ion interaction with pressure predicted earlier by Neaton and Ashcroft [11]. We speculate that with increasing pressure the electron-ion interaction in Li is enhanced to the extent that at 30 GPa a structural transition from fcc to a lower symmetry structure finally occurs. This transition removes, or at least relieves, the anomalous enhancement of the pseudopotential occurring in the fcc phase, allowing  $T_c$  to decrease with pressure due to dominant lattice stiffening effects, as in all canonical simple-metal superconductors [7]. As the pressure is increased further, however, the story repeats itself and  $T_c$  passes through a minimum at 50 GPa and increases again due to a renewed enhancement of the pseudopotential, only to fall again above 62 GPa following a further symmetry lowering phase transition. To test this scenario, detailed electronic structure calculations for the phases actually present at low temperatures would be very useful.

The anomalous behavior of  $T_c(P)$  for the “simple” *s,p* metal Li arises from the close proximity of the electron cores of neighboring ions under high compression. This situation will not be relieved, and Li allowed to revert to its former free-electron-like behavior, before such astronomically high pressures (far higher than those in the present experiment) are applied as to break up the atomic shell structure itself, resulting ultimately in a Thomas-Fermi electron gas.

To further characterize the superconducting state of Li, in run 2 we subjected the sample to dc magnetic fields up to 260 Oe. In the inset of Fig. 4,  $T_c$  at 21.9 GPa pressure is seen to decrease from 5.95 to 5.21 K when a field of only 200 Oe is applied, yielding the initial critical field slope  $(dH_c/dT)_{T_c} \approx -270$  Oe/K. Since the applied fields are insufficient to directly determine the critical field at 0 K,  $H_c(0)$ , from the present data, we use the expression  $H_c(0) = -\frac{1}{2}T_c(dH_c/dT)_{T_c}$ , derived from the standard empirical relation  $H_c(T) = H_c(0)[1 - (T/T_c)^2]$  [15], to obtain the estimate from the 21.9 GPa data that  $H_c(0) \approx -\frac{1}{2}(5.95 \text{ K})(-270 \text{ Oe/K}) = 800$  Oe. Critical field data  $H_c(T)$  at eight further pressures were obtained, five of which are shown in Fig. 4. In the pressure range 20 to 24 GPa the values of  $(dH_c/dT)_{T_c}$ ,  $H_c(0)$ , and  $T_c$  for Li are comparable to those found for canonical type I simple-metal superconductors like Hg and Pb where  $(dH_c/dT)_{T_c} \approx -198.2$  and  $-237.3$  Oe/K,  $H_c(0) \approx 412$  and 803 Oe, and  $T_c \approx 4.15$  and 7.195 K, respectively [16,17]. For  $P < 30$  GPa, the evidence that Li is a type I superconductor is thus quite compelling, although we cannot exclude the possibility of very weak type II

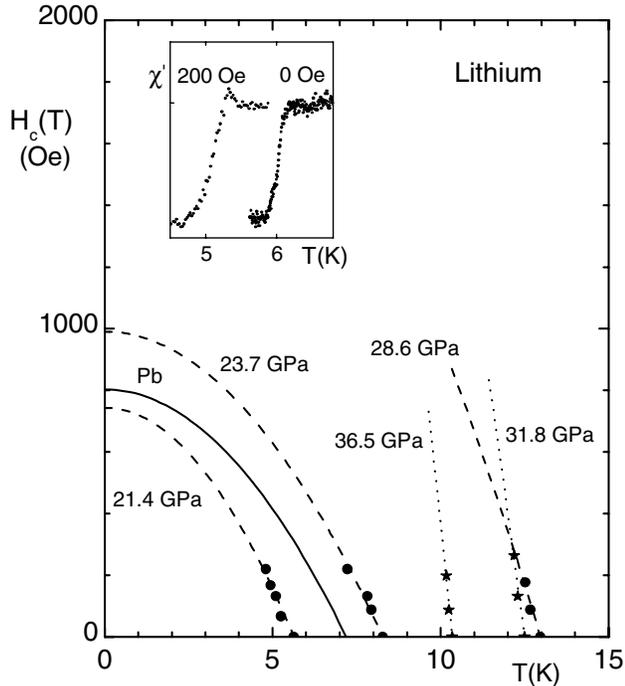


FIG. 4. Data points (●, ★) give to 220 Oe the critical magnetic field  $H_c$  versus temperature at various pressures for superconducting Li. Solid, dashed, and dotted lines are obtained using the empirical expression  $H_c(T) = H_c(0) \times [1 - (T/T_c)^2]$  to allow fits to the present data for Li in comparison to ambient-pressure data for Pb. For  $P = 28.6, 31.8,$  and  $36.5$  GPa we find  $H_c(0) \approx 2400, 5000,$  and  $4500$  Oe, respectively. The inset shows ac susceptibility data at 21.9 GPa for applied magnetic fields of 0 and 200 Oe.

behavior. All known ambient-pressure simple-metal ( $s,p$  electron) superconductors are type I if in a pure and strain-free condition.

For pressures slightly above versus slightly below 30 GPa, it is interesting to note that the initial slope  $(dH_c/dT)_{T_c}$  increases approximately twofold, likely signaling a comparable increase in  $H_c(0)$ . An abrupt change in  $(dH_c/dT)_{T_c}$  and/or  $H_c(0)$  would be consistent with the occurrence of a structural phase transition at 30 GPa. Since for type I superconductivity we have the relation  $H_c(0) \approx \frac{1}{2}[\Delta(0)]^2 N(E_f)$  [15], such an increase in  $H_c(0)$  could arise from an increase in the magnitude of either the superconducting gap  $\Delta(0)$  or the density of states  $N(E_f)$ . Alternatively, the phase transition at 30 GPa may create lattice defects which lead to weak type II behavior and an increase in the (upper) critical field.

Shimizu *et al.* [4] reported from resistivity measurements at 34 GPa, where  $T_c \approx 7$  K, that  $H_c(0) \approx 30000$  Oe, a value  $6\times$  larger than the maximum value of  $H_c(0)$  estimated in the present experiment. This high value of  $H_c(0)$  clearly points to type II superconductivity for their Li sample. Since in their experiment the direct contact of the Li sample with the diamond anvils and stiff gasket gen-

erated relatively large shear stresses, it is conceivable that the resulting plastic deformation led to a high density of defects with a sharp reduction in the electronic mean-free path, thus promoting type II behavior.

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