Superconductivity in lithium below 0.4 mK at ambient pressure

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Elements in the alkali metal series are regarded as unfavourable for superconductivity due to their monovalent character.[1,2] The superconducting transition at temperatures as high as 20 K recently found in compressed lithium,[3-6] the lightest alkali element, is considered to occur due to pressure induced changes in the conduction-electron band structure.[6-12] The condition at the ambient pressure in lithium had remained unresolved, both theoretically and experimentally.[11-16] Here we report that lithium is a superconductor also at zero pressure at extremely low temperatures below 0.4 mK. This is the lowest superconducting transition temperature for any pure metal ever observed. Lithium, as a particularly simple host for the conduction electron system, represents an important case for any attempts to classify the superconductors and transition temperatures, especially in judging if any nonmagnetic configuration can be assumed to exclude superconductivity down to zero temperature. Such a fundamental system provides a stringent test case for already highly developed computational methods in predicting the transition temperatures from first principles. Furthermore, the combination of extremely weak superconductivity and relatively strong nuclear magnetism in lithium would evidently lead to mutual

competition between these two ordering phenomena under suitably prepared conditions.[17,18]

The Fermi gas of conduction electrons in any metal is forced to a state with high energy content, of the order of thousands of kelvins, due to the Pauli exclusion principle. The degenerate state is susceptible to symmetry breaking phase transitions lowering the ground state energy due to even weak interactions between the electrons. Therefore, most metals develop either a magnetic or a superconducting state at low temperatures, usually at around kelvin range. The alkali metals sustain the degenerate state to an exceptional extent, which stems from the nearly ideal character of these monovalent metals. Since mutual interactions, no matter how weak, still exist in the condensed matter host, there is a possibility to test the fundamental question if any real conduction electron system can remain degenerate to zero temperature.

Until now, no alkali metal was known to become superconducting in its bulk form at the ambient pressure, while lithium was expected to be the best candidate in this group for showing such a phase change at a sufficiently low temperature.[13,14] Earlier experiments down to 4-5 mK failed to provide any indication of a superconducting state in lithium.[15,16] We cooled down our samples in an external field less than 20 nT to a temperature of 0.1 mK by means of a copper nuclear demagnetization refrigerator.[19] Susceptibility measurements showed superconducting transitions in several bulk lithium samples below 0.4 mK at zero pressure. The setup for the sample environment and the susceptibility measurement is illustrated in Fig. 1.

Two conditions are most critical, besides the sufficiently low temperature, to bring about the superconducting state with extremely low critical temperature. First, the sample material must be sufficiently clean with respect to magnetic impurities, as they easily disturb the electron pairing necessary for the superconductivity. The exact relation between the impurity concentration and the suppression of the critical temperature depend on the host and on the impurity, but as a rule of thumb one may assess that the T_c is lowered on the order of 0.01-0.03 mK/ppm. Note that this effect is independent of the absolute magnitude of the critical temperature. Thus, as little as 10 ppm of iron, for example, could seriously shift the transition in relative terms for a metal with a low T_c to begin with. The manufacturer of the raw lithium we used (Alfa Aesar, Johnson Matthey GmbH, Karlsruhe, Germany) stated maximum magnetic contamination of 4 ppm for this particular batch. For more details on the purity, see Ref. [18].

The second imperative is that of good shielding from any ambient magnetic field, since a low transition temperature is bound with a low critical magnetic field also. This demand is strengthened by the tendency of supercooling of the normal state in any finite magnetic field: already one thousandth of the field of earth can suppress a sub-millikelvin transition all the way down to zero temperature. In fact, this feature dictates the way a measurement is performed in practice, as it is not feasible to make a temperature scan in a constant magnetic field, but one must do a field scan at a constant temperature. Supercooling is then manifested by the difference in the fields where the normal state disappears and appears again. Also, since the normal state can persist far below the critical temperature, the actual T_c must be estimated from an extrapolation.

Specific to lithium is its high reactivity together with some peculiar low temperature properties. Capsulation with thin sheets of copper was found to keep the lithium specimens intact and to provide good thermal coupling to them.[20] When cooling from room temperature, the lattice of lithium transforms at about 80 K to a somewhat ambivalent structure with supposedly predominant rhombohedral 9R symmetry.[21-23] It is then important to assure that the studied low temperature properties reproduce upon repeated thermal cycling, which was the case in all essence during this study. Attention was paid to cool each specimen in a similar fashion: in about 20 hours from 100 to 10 K, where about 10 hours was spent close to the liquid nitrogen temperature (the transition region for Li).

The samples were always cooled as pairs of two separate entities within the single measurement setup, see Fig. 1. A total of three pairs were examined. We begin the detailed description from the last sample pair, which helps interpreting the results of the other ones.

The susceptibility signal for the last pair during slow magnetic field sweeps at a few values of temperature below the T_c are shown in Fig. 2. The estimated critical temperatures for the two separate halves were very close to each other, 0.18 and 0.19 mK. The constant signal levels in the normal state above a certain threshold field as well as in the evidently perfect Meissner state close to the zero field are clearly distinguishable in Fig. 2, but the transition region in between deserves some further discussion. When such field sweeps were repeated at a constant temperature several times back and forth, the drop-down edge varied somewhat in position, depending on the extent of supercooling. Also the rise-up edge showed some variation, although it might naturally be thought of as the signature of returning back to the normal state, *i.e.*, the critical field $B_c(T)$. However, the small positive susceptibility anomaly at the edge of the transition seems also to be related to the superconducting state, as it was never observed else than at the vanishing point of the superconductivity. Also, the small outer edge, where the susceptibility finally returns to the normal state level was the most reproducible point on the field axis across the whole pattern. For these reasons, it seems plausible to associate this particular point as the true $B_c(T)$, although such a choice would not seem obvious otherwise. It is not clear if this anomalous region of positive signal can be explained by an ordinary intermediate state of a superconductor. In the following, it is shown that a similar anomaly was identifiable on the other lithium samples, too.

The results for an earlier sample pair are summarized in Fig. 3 as a colour coded contour diagram of susceptibility. There are multiple regions of both positive and negative values of susceptibility which suggests, according to the interpretation above, that there were at least three distinct transitions with the T_c's extrapolated to 0.43 mK, 0.25 mK, and 0.16 mK, successively. As this pattern is far more complex than expected, we initially thought this peculiar response not indicating superconductivity down to 0.1 mK, as reported in Refs. [17] and [18]. However, in view of the further results on similar samples, as discussed above, this conclusion must be revised. We may only speculate about the reasons for observing more than two transitions (one should appear for each half) with such a large spread in temperature. Obviously, the sample is split into crystallites with distinctly different properties. The critical temperature could be altered by an uneven distribution of magnetic impurities in the sample, and then the highest one observed must be considered as the one closest to the actual critical temperature of pure lithium. Alternatively, it is plausible that the lattice structure varied across the sample due to the martensitic phase transition undergone at about 80 K to a low temperature structure, which is not entirely well defined.[21-23] This may be influenced by a possible residual stress at the Li-Cu interface due to different thermal contraction of the two metals.

Yet another sample pair was investigated with no lithium in it in order to perform a control measurement. We felt necessary to make explicitly sure that the peculiarities we observed were really produced by lithium, not anything else that was contained in the measuring system. After all, the measuring coil enclosed nearly equal amounts of copper and lithium and there was also a small amount of Stycast epoxy securing the sealing of the capsules. For this purpose, the setup was prepared exactly in the similar fashion as for the other specimens, except that no lithium was put into the capsules. This run produced a perfectly flat response with no observable deviation from the zero signal. This also proves that copper metal is not a superconductor at least above 0.1 mK.

In conclusion, the series of experiments on three pairs of samples show that lithium is a superconductor at ambient pressure, albeit with an extremely low transition temperature. The observed value $T_c \approx 0.2$-0.4 mK is the lowest among pure bulk superconductors, and is comparable only to that of rhodium with $T_c \approx 0.5$ mK. This is an estimated value for pure Rh, while magnetically contaminated specimens show $T_c \approx 0.2$-0.3 mK.[24,25] Pure gold has been estimated to become superconducting at 0.1 mK on the basis of studies on Au-In alloys, but no direct verification of this exists.[26]

It is not clear if the transition temperature of Li would increase monotonously to the values in the kelvin range observed at very high pressures, or if the pressure would first quench the superconductivity and then make it reappear once the lattice transformations take place at high pressures.

Our samples were of natural composition with about 92 % of ^{7}Li. Since this is one of the lightest elements, the isotope effect would be exceptionally strong, suggesting a definite difference between samples made of pure isotopes ^{6}Li and ^{7}Li. Unfortunately, any precise comparison would suffer from the vulnerability to the smallest amounts of magnetic impurities.

As a nearly free-electron system, lithium constitutes an important test case for any approach to theoretically determine the critical temperature of superconductivity. It is noteworthy, that a calculation based on hierarchy of energy scales of electrons and phonons and of their interactions actually prognosticated the value we experimentally found for lithium.[14] It is evident that there is a strong depression of T_c due to electron-

electron repulsion effects, since the phonon coupling alone would obviously be sufficiently strong to create superconductivity at around one kelvin. The lithium system also elucidates the speculations about whether an electron gas can spontaneously develop intrinsic superconductivity without the assistance of phonons by virtue of screening, exchange and correlation effects.[14] Current understanding is that a simple one band system is not capable of that. This view is in accord with the extremely low transition temperature of natural lithium observed here.

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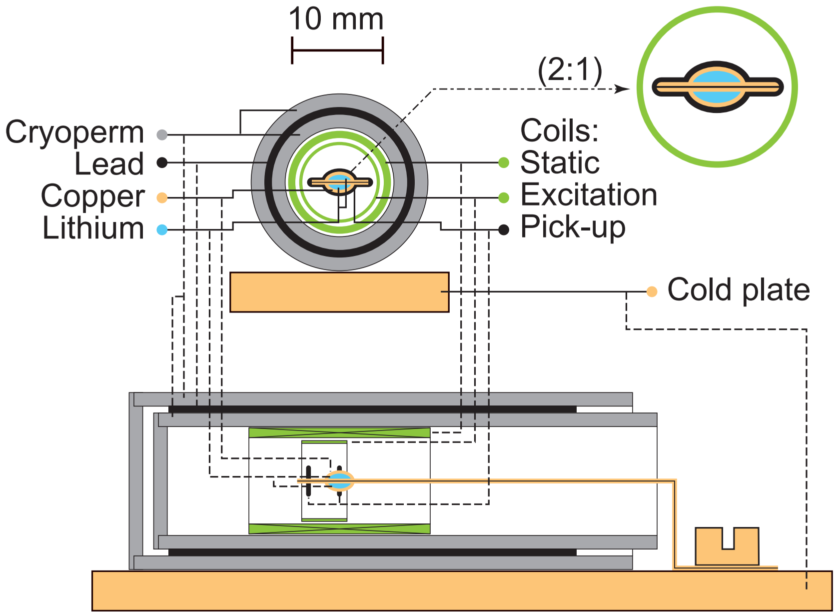
Figure 1 Schematics of a lithium sample pair, magnetic shields and the measuring coil system. The arrangement is shown both along the axis (upper left) and as cut from the side (below). Pieces of lithium metal were capsulated into pockets of thin copper foils, which also made the thermal link to the refrigerator cold plate. Handling of lithium was performed in an argon glove box with precautions to avoid any contamination of the sample material. A pick-up coil for a SQUID susceptometer was wound directly on a pair of two identical samples (see the magnification at the upper right), which were then placed into the cylindrical shields and solenoids. The magnetic shields consisted of two layers of high-permeability material (Cryoperm 10) with a superconducting lead cylinder in between to give nearly total immunity to external fields. The SQUID detection was made with very small excitation amplitude (some nanoteslas) at the frequencies 3-17 Hz. A static field for the measurement could be created by another solenoid inside the shields. The assembly was cooled down with three different pairs of samples to about 0.1 mK with a field less than 20 nT.

Figure 2 Observation of the Meissner state indicating superconductivity in lithium. The susceptibility is plotted as a function of the current generating the static magnetic field (~ 10 mT/A) at three values of temperature below the $T_c \approx$ 0.18 mK. Each data set is shifted vertically for better visibility and the arrows show the direction of the field sweep. When the field is reduced from above the critical value, the samples remain in a metastable normal state until rather close to the zero field (supercooling). Then they enter the perfect Meissner state, which, however, is not maintained quite up to the critical field. Just before that the susceptibility is positive over an interval, whose width depends on temperature. The width of the Meissner state varied a little bit in repeated sweeps but the position of the drop from the small positive signal to the background level was always well reproduced, which we take as the marking of the transition to the normal state. At the highest temperature here displayed (red curve), one half of the sample remains in the metastable normal state, so that the signal drops by just half of that at the lower temperatures. As expected, the transition occurs at ever higher field as the temperature is reduced.

Figure 3 Phase diagram for another pair of lithium samples. Susceptibility contour diagram is displayed as a function of temperature and the current generating the static magnetic field (~ 10 mT/A). Light green corresponds to signals beyond resolution (~ zero susceptibility), light blue represents small positive signal, and the red tones show negative values (Meissner state). These samples were roughly half in size compared to those investigated in Fig. 2. Also the pick up coil for the SQUID susceptometer was less effective resulting in poorer signal to noise ratio. Nevertheless, similar features to those in Fig. 2 are clearly identifiable. The outmost edge of the positive susceptibility is taken as the critical field trajectory (blue dashed line), which is extrapolated to the critical point by the standard form $B_c(T) = B_c(0)[1 - (T/T_c)^2]$. This interpretation is supported by the fact that the supercooling phenomena were encountered only after an excursion beyond this line, indicating that the superconducting state still existed in the sample within this region. Three distinct anomalies are seen, which is apparently due to non-homogeneity of the samples. Above 0.3 mK, where the transition seemingly disappears, only the metastable normal state is observed below the T_c due to supercooling. The metastable state can extend that far due to the small energies involved.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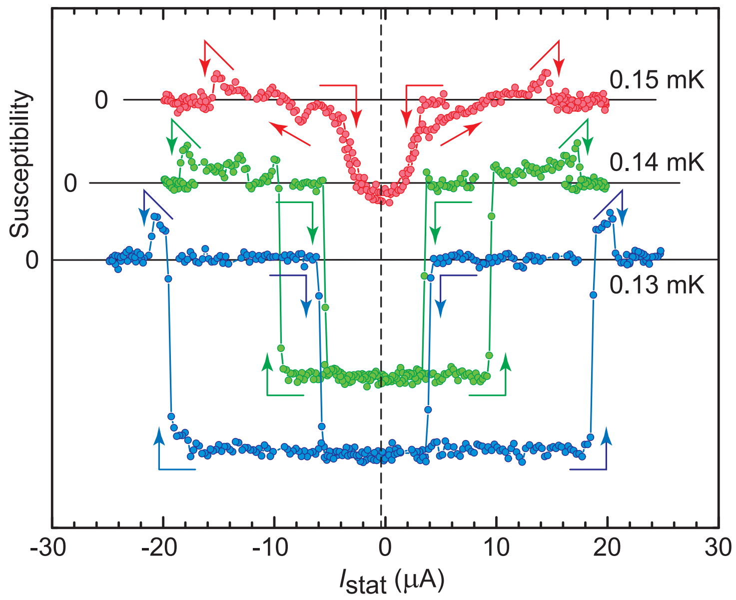
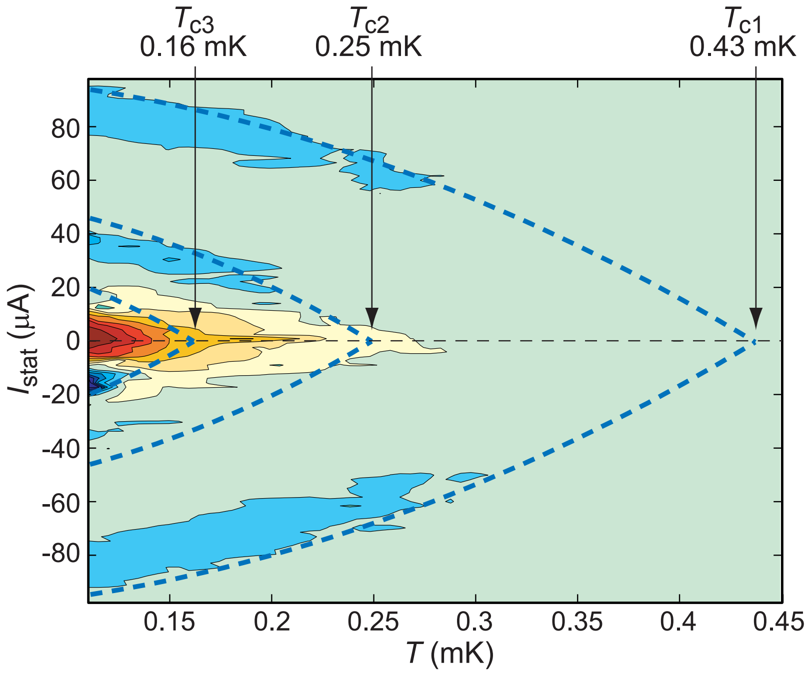


0.15 mK
0.14 mK
0.13 mK
0
0
0
Susceptibility
-30
-20
-10
0
10
20
30
I_{stat} (μA)


T_{c3}
0.16 mK
T_{c2}
0.25 mK
T_{c1}
0.43 mK
80
60
40
20
0
-20
-40
-60
-80
I_{stat} (μA)
0.15
0.2
0.25
0.3
0.35
0.4
0.45
T (mK)