Search for Superconductivity in Lithium

K. M. Lang,[1] Ari Mizel,[1,2] J. Mortara,[1] E. Hudson,[1] J. Hone,[1,2]
Marvin L. Cohen,[1,2] A. Zettl,[1,2] and J. C. Davis[1]

[1] *Department of Physics, University of California at Berkeley, Berkeley,
California 94720-7300, USA*
[2] *Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley,
California 94720, USA*

*We report on the results of a search for superconductivity in Li. We find no
evidence for the predicted transition to superconductivity at any temperature
down to 5 mK in magnetic fields down to 0.4 μT. However, an unexpected
Curie–Weiss temperature dependence in the magnetic susceptibility is observed.
We discuss the possibility that this signal arises from the Li itself, the
possibility that it arises from Kondo behavior, and the implications of the
effect for the predicted T_c of Li.*

I. INTRODUCTION

Theory has long predicted,[1,2] that Li should become superconducting at accessible temperatures in the millikelvin range. Several experiments have searched for this effect, the most recent in a refrigerator capable of reaching 4 mK,[3] but none have found evidence for a superconducting transition. Recent predictions based on increasingly sophisticated calculations continue to indicate that Li should be a superconductor at attainable millikelvin temperatures.[4,5] Accordingly, the objective of the research described in this paper was to search for a superconducting transition in Li at temperatures down to 5 mK.

II. EXPERIMENTAL METHODOLOGY

The experiment is designed to search for the Meissner effect which is manifest as a large diamagnetic change in the magnetic susceptibility (χ) at T_c, indicating a superconducting transition. The apparatus uses DC SQUID based detection of flux changes in an astatic coil-pair[6] arrangement. We discuss below in more detail how we ensure cooling of the sample and also the methods we use to measure its temperature and susceptibility.

The sample is attached to the mixing chamber stage of a dilution refrigerator[7] capable of reaching 5 mK. To ensure that the Li sample reaches these temperatures, it is necessary to have a robust thermal contact between the sample and the refrigerator. If pressed against another metal, Li may make too poor a thermal contact to achieve mK temperatures since its surface oxidizes rapidly. Therefore, melting the Li in an anaerobic environment onto a metal surface which it wets, and then cooling that surface, ensures a better thermal contact to the Li than a press contact. We determined by experiment that Li wets Ag, but not Cu, Au, or Pt. Accordingly, our sample holder is a cylindrical Ag cup with a 0.64 mm diameter Ag wire welded to the closed end. Our Li sample[8] is melted into the sample holder, and the open end is capped with Torrseal,[9] while all these components are enclosed in an Ar atmosphere glove box. To make thermal contact from the cup to the refrigerator, we hold the Ag wire between Cu press plates screwed to the mixing chamber. A similar system is used to make thermal contact from a W single crystal,[10] whose use in calibration is described below, to the mixing chamber. This method of making a robust thermal contact from the dilution refrigerator to the Li and W samples helps ensure that they indeed reach the temperature of the mixing chamber.

A four wire resistance bridge[11] measurement of a ruthenium oxide (RuO_2) resistance thermometer[12] is used to measure the temperature of the mixing chamber and thus of the Li sample. For temperatures below 60 mK, a ^{60}Co nuclear orientation thermometer[13] is used as a primary calibration of the RuO_2. The W superconducting transition provides a single fixed temperature point to verify thermal contact between the ^{60}Co thermometer and the experimental apparatus that contains the W and the Li samples. For temperatures above 50 mK, a calibrated Ge resistance thermometer[14] is used to calibrate the RuO_2. We thus obtain a complete calibration curve of resistance versus temperature for our RuO_2 thermometer.

To measure the magnetic susceptibility of the Li sample, we use the apparatus depicted in Fig. 1, which shows the geometry of the various components of the apparatus. The innermost astatic coil-pair (a) is wound with one length of 0.23 mm diameter CuNi clad NbTi wire on a Stycast 1266 form with one side of the pair having opposite chirality but matching inductance to the other. The leads from this astatic pair run through Pb-Sn shielding tubes to connect to the input coil of a DC SQUID.[15] The inductance of one side of the coil-pair is closely matched to the input inductance of the DC SQUID. In one side of the coil-pair we place our Li sample (b) which is thermally connected to the mixing chamber by a Ag wire. In the other side of the coil-pair we place a W single crystal (c) which is used for calibration and which is thermally connected to the mixing chamber via a Cu wire. Although the Li and/or W samples may be gently touching the

inner Stycast form there is effectively only thermal contact between these samples and the mixing chamber because the thermal conductivity of their Cu/Ag connections to the mixing chamber is $\sim 10^4$ times greater than that of the Stycast.[16]

The inner coil-pair is surrounded by a uni-directionally wrapped coil also on a Stycast 1266 form (d). The leads from the uni-directional coil are attached to a current supply which enables us to control the magnetic field in the sample region. Surrounding all the coils is a cylindrical Pb super-conducting shield (e). All the coils and the Pb shield are inside a hollow Cu cylinder (f) which holds the parts together and also provides cooling for
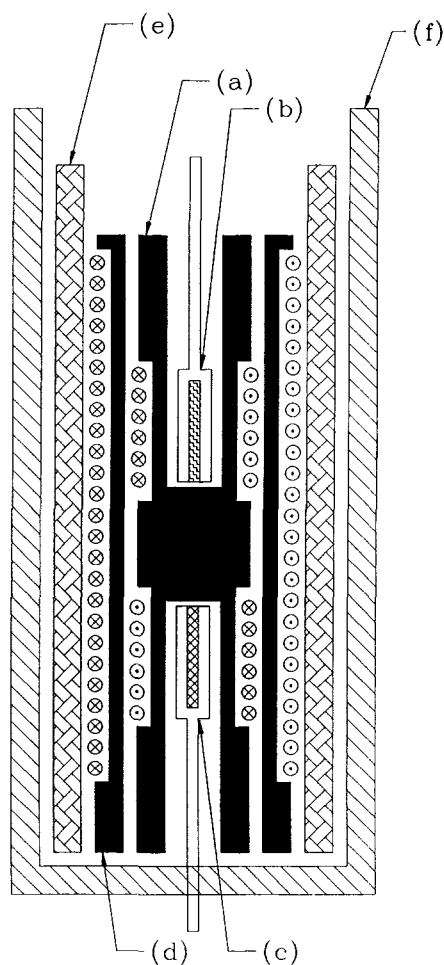

Fig. 1. Schematic drawing of the experimental apparatus showing the Ag enclosed Li sample (b) and the Cu enclosed W single crystal (c) inside the astatic coil (a) whose leads connect to the SQUID (not shown). The samples and astatic coil are inside a coil (d) capable of making a magnetic field in the sample region and a Pb cylinder (e) used to shield stray magnetic fields. Everything is held in a Cu container (f) which is in good thermal contact with the mixing chamber of a dilution refrigerator.

the whole apparatus since it is in good thermal contact with the mixing chamber of the refrigerator.

The apparatus described above enables us to measure a change in the magnetic flux threading the samples in the astatic coil-pair. We use the following equation to convert magnetic flux changes as measured at the SQUID into magnetic susceptibility changes of the Li sample.

$$\Delta\chi = \frac{\alpha\Delta\phi}{(I - I_0)} \tag{1}$$

In this equation, $\Delta\phi$ is the change in magnetic flux through the astatic coil-pair (a) as measured at the SQUID; I is the current in the outer coil (d); I_0 is the outer coil current needed to cancel the trapped field in the region of the samples; and α is a calibration constant which depends upon the geometrical coupling of a sample to the astatic coil-pair and the properties of the flux transformer between the coil-pair and the SQUID. Since the W and Li samples are close to being geometrically identical and in nearly identical coils of the astatic pair, α and I_0 are experimentally determined by measuring the size of the flux signal $(\Delta\phi)$ for the W superconducting transition at several different values of I. The W transition can be identified because it occurs at 15.5 mK, the known T_c of this material. We determine a value for I_0 by plotting $\Delta\phi$ for the W transition versus I, and then we take I_0 to be that value of I for which $\Delta\phi$ is zero. $(I - I_0)$ is then proportional to the net field in the region of the sample. Once I_0 is known, we can determine α by recognizing that the measured flux change for the W sample during a superconducting transition is due to a susceptibility change of $\Delta\chi = -1$.[17]

To search for superconductivity in Li, and to map the Curie–Weiss paramagnetic signal as described below, we carried out a series of experiments in which we varied the temperature of the Li sample from 5 mK to 500 mK and measured subsequent changes in its magnetic susceptibility as a function of temperature. Data taken on both warming and cooling and using two different Li samples all show consistent results. Searches for superconductivity were carried out at very low fields down to $0.4\,\mu$T, whereas mapping of the Curie–Weiss paramagnetic signal was carried out at larger fields up to ± 0.1 mT to enhance the sensitivity of the SQUID based system. Quoted values for magnetic fields are always net field, which is the sum of the trapped field ($\approx 20\,\mu$T) and the field created by the outer coil.

Our sample preparation together with our experimental setup enables us to both cool the sample to 5 mK and to measure its susceptibility with

great sensitivity. Not only do we make great efforts in the sample preparation to ensure good thermal contact, but we also use a DC SQUID based detection system which does not induce eddy current heating as an AC detection system might do. The SQUID based detection system also means that we have a signal to noise ratio of ~ 1100 in a magnetic field of $0.29\,\mu$T for measuring the W superconducting transition. This is an improvement by a factor of ~ 25 over previous experimental measurements. This increased sensitivity is not necessary to see a superconducting transition; however, it allows us to observe the low temperature Curie–Weiss behavior (discussed below) that we see in the susceptibility of the Li sample.

III. RESULTS

We found no evidence for a Meissner superconducting transition in the Li down to temperatures of 5 mK and in magnetic fields down to $0.4\,\mu$T. We did observe an unexpected Curie–Weiss temperature dependence in the susceptibility of the Li sample. To ensure that this signal came from the Li and not from any other part of the apparatus, we measured the susceptibility for the apparatus with all elements unchanged except for the Li sample, which was replaced by an empty Ag cup. The comparatively small background susceptibility thus obtained was subtracted from the
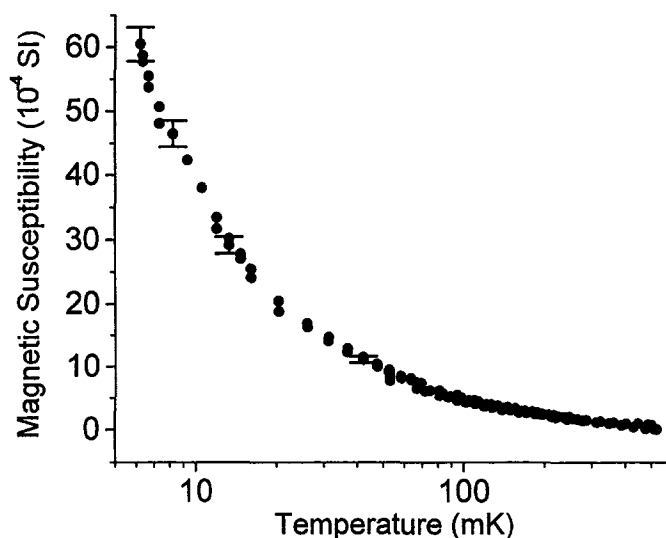

Fig. 2. Magnetic susceptibility of Li sample versus temperature. Representative error bars are shown on several points. These measurements represent both warming and cooling data and were taken in an external field of $92\,\mu$T.

data taken with the Li in place. With our experimental setup we are only
able to measure temperature dependent changes in the susceptibility.
Therefore, to produce the absolute susceptibility curve shown in Fig. 2, we
used the background subtracted data and set the susceptibility obtained at
the highest temperature equal to the known temperature independent Pauli
paramagnetic susceptibility.[18] It can be seen in the figure that the suscep-
tibility is relatively temperature independent at those highest temperature
points. Thus Fig. 2 gives the absolute susceptibility of our Li sample as a
function of temperature.

IV. DISCUSSION

The failure of our sample to undergo a superconducting transition
may be linked to the unexpected Curie–Weiss temperature dependent
susceptibility. It is therefore important to investigate the origin of this
paramagnetic behavior.

It is difficult to see how the Li itself could generate the measured
susceptibility signal. The 2s conduction electrons of Li form a degenerate
Fermi gas with a bandwidth of approximately 3 eV.[2, 5, 19] Because of the
degeneracy, the conduction electrons should exhibit a small, temperature
independent Pauli paramagnetic susceptibility which has been measured to
be 0.27×10^{-4}.[18] This expectation applies regardless of whether the electron
gas possesses a usual paramagnetic ground state or even a more exotic
ground state such as a spin-density wave. Thus the paramagnetism of the
conduction electrons cannot account for our measured results by standard
models. In addition, the 1s core electrons of the Li are energetically trapped
in spin singlet states and should make only a small diamagnetic contribu-
tion to the susceptibility. Finally, although the Li nuclei should produce a
temperature dependent paramagnetic susceptibility, we calculate that this
signal would be smaller than our observed signal by a factor of ~ 100.

Since there is no standard mechanism for the Li itself to produce the
observed paramagnetism, we now consider the possibility that the signal is
caused by impurity atoms. The electrons of a transition metal impurity
could act like localized free spins, exhibiting Kondo behavior[20, 21, 22] by
producing a susceptibility that follows the Curie–Weiss form:

$$\chi = \frac{C}{T + \theta}.$$ (2)

As Fig. 3 shows, our experimental data fits this form with $\Theta \approx 2.4$ mK. We
note that the linear relation seen in Fig. 3 between inverse susceptibility
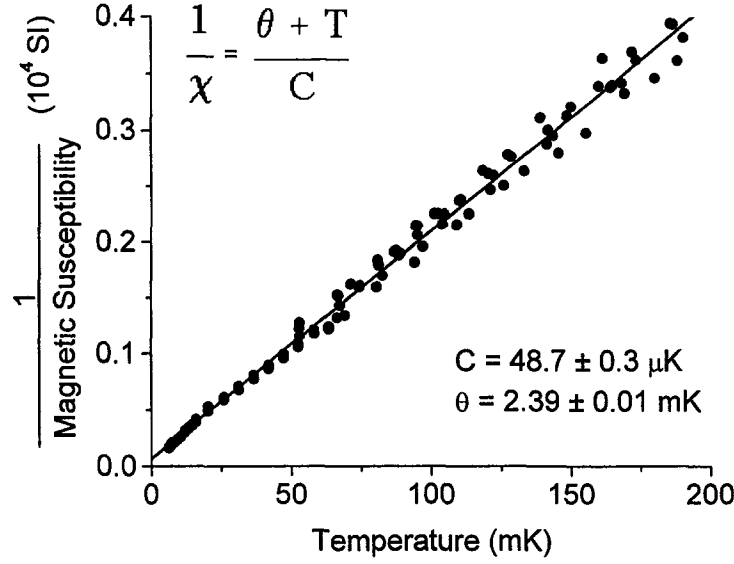and temperature provides an independent confirmation of the existence of

$$\frac{1}{\chi} = \frac{\theta + T}{C}$$

$C = 48.7 \pm 0.3\ \mu K$

$\theta = 2.39 \pm 0.01\ mK$

Fig. 3. Data from Fig. 2 shown as inverse magnetic susceptibility versus temperature. The line shown indicates a fit of the data to the Curie–Weiss law. The fit parameters and errors given in the figure were obtained using statistical methods outlined in Ref. 30.

good thermal contact between the Li sample and the RuO_2 resistance thermometer at the mixing chamber for all temperatures.

Following Heeger[21] we take $\Theta = 4.5T_K$ and the following definition of the Kondo temperature:

$$T_K = T_F \exp\left(-\frac{1}{2\rho\ |J|}\right). \tag{3}$$

where J is the exchange coupling, T_F is the Li Fermi temperature, and 2ρ is the density of states per atom (including both spin directions) at the Fermi level. Taking the parameters 2ρ and T_F as those of the 9R phase of Li,[5] we find that $J \sim 0.1$ eV. We may use the following expression:[21]

$$C = \frac{n\mu_0\mu_{eff}^2}{3.66k_B} \tag{4}$$

to calculate the impurity concentration necessary to produce a Curie–Weiss paramagnetic signal of the observed magnitude. Here n is the impurity concentration and μ_{eff} is the impurity effective magnetic moment. Taking the case of Fe in Li, for which $\mu_{eff} \sim 3\mu_B$,[23, 24] we find that a mass fraction of ~ 450 ppm of Fe is required to account for the size of our signal.

The calculated mass fraction of ~ 450 ppm is substantially higher than the 13 ppm for Fe which was measured in an atomic emission spectroscopic analysis of the impurities in our Li sample. In addition, the value we found for J is smaller than one might expect for a transition metal impurity in Li[21, 24] for which J values are usually on the order of 1 eV. One could speculate that this low J results from the Fe residing on the surface of the sample. If the Fe were on the Li surface, its magnetic moment could be close to the free atom value of $\mu = 6.708\mu_B$. In this case a somewhat smaller mass fraction of ~ 90 ppm of Fe would be required to account for the magnitude of the observed effect. Alternatively, one might imagine that Fe together with a number of other transition metal impurities participate in generating our signal. Our impurity analysis concentrations are reported in an endnote.[25] Finally, one might propose that non-transition element impurities cause the signal; however, calculations suggest that sp impurities such as N, O, C or Si are unlikely to retain their magnetic moments in a Li host.[26]

Whatever its origin, intuitively it seems that a paramagnetic signal like the one we observed should be incompatible with traditional BCS superconductivity. For instance, if our measured paramagnetic susceptibility is indeed caused by magnetic impurities, the magnetic scattering associated with these impurities could have prevented a superconducting transition.[27] The complete suppression of T_c due to magnetic scattering occurs when the effective pair-breaking energy is on the order of the zero temperature energy gap. Estimating the pair-breaking energy with $J \sim 0.1$ eV, we find that superconductivity should be completely suppressed if the T_c of pure Li is less than ~ 10 mK.

The absence of a superconducting transition in our Li sample could be linked, as we discussed above, to the observed paramagnetic signal; however, supercooling is another possible explanation for its absence. Supercooling has been encountered in past searches for superconductivity in other elements at mK temperatures.[29] Although we have no evidence either for or against this possibility, it is not impossible that supercooling could have prevented observation of the superconducting transition if $T_c \sim 10$ mK.

V. CONCLUSIONS

We have cooled Li to 5 mK in fields down to $0.4\,\mu$T and have seen no evidence for the Meissner effect accompanying a superconducting transition in the sample. An unexpected Curie–Weiss temperature dependence of the magnetic susceptibility of bulk Li at low temperatures was observed. We have discussed the possibility that the signal originated in the Li itself and

the possibility that it originated from impurities in the sample. Further experiments are necessary to elucidate the origin of the paramagnetic signal and to clarify the question of superconductivity in Li.

ACKNOWLEDGMENTS

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5. Y. Jin and K. J. Chang, *Phys. Rev. B* **57**, 14684 (1998). These authors predict T_c for Li in the range: $92\,mK > T_c > 2.4\,mK$ for no spin fluctuations and on the order of $96\,\mu K$ when considering spin fluctuations.
6. An astatic coil-pair is a solenoid wound with a single wire, first in one direction and then in the other.
7. Modified Kelvinox 400 by Oxford Instruments, Oxon, England.
8. Li is stock number 10769 by Alfa Aesar, Ward Hill, Massachusetts. The Li we use contains the naturally abundant mix of isotopes and has a 99.9% purity rating on a metals basis which means that the manufacturer guarantees no more than 0.1% of the sample consists of metallic impurities. Li with a significantly higher purity rating than this is not commercially available. We performed our own impurity assay for common contaminants. See the Discussion Section for more details.
9. Torrseal by Varian Vacuum Products, Lexington, Massachusetts. Torrseal is an epoxy whose main ingredients are epoxy resin and talc. According to the manufacturer, it contains no magnetic material.
10. The W sample used was an ultrapure single crystal obtained from NIST specifically for calibration and thermometry.
11. LTC-20 Temperature Controller by Conductus, San Diego, California.
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14. GR-200A-30 Germanium Resistance Thermometer by Lake Shore Cryotronics, Inc., Westerville, Ohio.
15. SP 550 DC SQUID system by Quantum Design, San Diego, California.
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25. Results of an impurity analysis of our Li sample done by atomic emission spectroscopy are hereby provided together with the free atom magnetic moments given for the reader's convenience.

element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Nb	Mo
concentration $(\mu g/g)$	< 10	17	< 10	< 2	< 2	13	< 2	< 2	< 10	< 10
mag. moment (μ_b)	1.549	1.632	0.775	6.928	5.916	6.708	6.633	5.590	2.887	6.928

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