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Publication Date
1970-08-01

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August 1970

UCRL-19650

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SEARCH FOR SUPERCONDUCTIVITY IN LITHIUM AND MAGNESIUM*

by

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Abstract

Recent theoretical work suggests that magnesium and lithium
should be superconducting in the millikelvin range of temperature.
We have cooled samples of each of these metals to a temperature
of 4 mK, measured by a gamma-ray anisotropy thermometer.
Although the magnetic field was less than 10^{-2} Oe, no super-
conducting transitions were observed. The use of a nuclear
orientation thermometer employing ^{60}Co in single-crystal (hcp)
cobalt is described.

INTRODUCTION

Recent advances in the theory of metals raise the possibility of reliably predicting the critical temperatures of superconductors from normal-state data. In particular, Allen and Cohen[1] have used a pseudo-potential method to treat the electron-phonon interaction for a number of metals, and shown that Mg and Li might be superconducting at experimentally accessible temperatures. A verification of their calculation by the discovery of superconducting transitions in these metals would be of sufficient interest to justify a search for superconductivity even though it is not possible to cover the whole of the temperature regions corresponding to the recognized uncertainty in the calculations. We have accordingly tested magnesium and lithium for superconductivity down to 4 mK. The results were negative, but they do serve to set limits for the parameters related to the critical temperature, and the experimental techniques may also be of some interest.

McMillan[2] has obtained accurate numerical solutions for the critical temperature of a superconductor using the Nambu-Gor'kov-Eliashberg formulation of the BCS theory and a particular phonon spectrum. The results were fitted to an expression of the form

$$\frac{T_c}{\omega_0} = \exp\left[\frac{-(1 + \lambda)}{\lambda - \mu^* - (<\omega>/\omega_0)\lambda\mu^*}\right] , \qquad (1)$$

the analytical solution obtained in a two-square-well approximation.
T_c is the critical temperature, ω_o is the maximum phonon frequency,
and μ^* is the coulomb pseudo-potential of Morel and Anderson.[3] The
electron-phonon coupling constant is

$$\lambda \equiv 2 \int_0^{\omega_o} \alpha^2(\omega) \, F(\omega) \, \frac{d\omega}{\omega} \; , \tag{2}$$

and $< \omega >$ is an average phonon frequency defined by

$$< \omega > \equiv (2/\lambda) \int_0^{\omega_o} \alpha^2(\omega) \, F(\omega) \, d\omega \; . \tag{3}$$

The phonon density of states is $F(\omega)$ and $\alpha^2(\omega)$ is an average of the
square of the electron-phonon matrix elements. The numerical solutions
of the gap equation were based on the phonon spectrum of Nb, and after
fitting to an equation of the same form as Eq. (1), McMillan obtained
the result,

$$\frac{T_c}{\Theta} = 0.690 \, \exp \left[\frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right] \; , \tag{4}$$

where Θ is the Debye temperature. The formula is not expected to be
sensitive to the details of the phonon spectrum for $\lambda < 1$ (the case
of interest here) and served as the basis for the predictions of T_c by
Allen and Cohen.

Allen and Cohen have calculated λ for the hexagonal divalent
metals beryllium, magnesium, zinc, and cadmium, using the known (except
for cadmium) phonon density of states and deriving the electron phonon
matrix elements from empirical pseudo-potentials that accurately fit the

extensive Fermi-surface data. Since the phonon interaction increases

the electronic heat capacity by the factor $(1 + \lambda)$, an empirical

value of λ can be obtained by comparing the experimental heat

capacity with band-structure calculations of the electronic density

of states. McMillan has also derived empirical values of λ from his

formula and known values of T_c (taking $\mu^* = 0.1$). The theoretical and

empirical values of λ are compared in Table I, reproduced from

Table V of Reference 1. The good agreement between the various values

of λ gives support to the underlying assumptions.

McMillan has suggested that $\mu^* = 0.1$ is a good approximation for

simple metals, but in the case of magnesium λ is small enough for the

predicted T_c to be relatively sensitive to errors in μ^*. Allen and

Cohen used the random phase approximation to calculate μ^* for beryllium,

magnesium, zinc, and cadmium. The values so obtained were too small,

but, on the assumption that the calculations gave relative values

correctly, they used the value of μ^* for zinc (known from the

isotope effect) to obtain $\mu^* = 0.16$ for magnesium. McMillan's equation

with $\mu^* = 0.16$ and $\lambda = 0.31$ gives $T_c = 0.02$ K for magnesium.

However, T_c depends exponentially on λ and μ^*, and the uncertainties

in these parameters estimated by Allen and Cohen are such that T_c might

be higher or lower by an order of magnitude (see Figure 3 of Reference 1).

The lowest temperature to which Mg has been previously investigated is

0.017 K.[4]

Similar internal checks on the parameters for lithium were not

possible for two reasons. First, the pseudo-potential used (selected

because it gave the lowest critical temperature) was that derived

from first principles by Goddard[5] who checked it with atomic energy level

data but not with Fermi surface data--of which there is very little.

Second, there is a martensitic phase transition in lithium at about 80 K

which results in some of the sample converting from the high-temperature

bcc phase to the low temperature hcp phase.[6] The calculations on

lithium were made using (a) the Goddard potential, screened by the

Lindhard dielectric function; (b) experimental bcc phonon dispersion

curves[7]; (c) the phonon renormalized mass m^* derived from specific

heat measurements[8] on samples for which the extent of the martensitic

transformation was not known and could only be estimated from other data[6,9];

and (d) values for λ, and the band-mass, m_b, derived self-consistently

from m^* and λ calculated using $m_b = 1$. Furthermore, the number

0.62 in Eq. (4) may be incorrect for lithium. For the alkali metals,

but not for most other metals, direct scattering processes are relatively

more important than umklapp processes and the transverse modes are less

strongly coupled than the longitudinal modes. This could raise the

value of $<\omega>/\omega_o$. Although the constant 0.62 was not derived by

calculating $<\omega>/\omega_o$, an increase in the expected value of $<\omega>/\omega_o$

suggests that the constant 0.62 could be larger. The lowest temperature

to which Li has been previously investigated is 0.08 K.[10]

These calculations suggest a reasonable probability for the occurrence

of superconductivity in magnesium at presently available temperatures

and that lithium is the most likely of the alkali metals to become

superconducting. The latter result is interesting since earlier

calculations of λ suggest the contrary.[11]

EXPERIMENTAL

Cryostat, field and susceptibility measurements

In this section we discuss all aspects of the experimental procedure

except for the nuclear thermometry which is discussed in detail in the

next section.

In order to observe a transition, both the temperature and magnetic

field must be sufficiently low. In Table IV we give the thermodynamic

critical fields at $T = 0$ calculated from the BCS model assuming

the known transition temperatures for beryllium[4] and tungsten[12] and

our lowest operating temperature for magnesium and lithium.

The cryostat system used for this experiment was similar to that

described by Brewer.[13] It consisted of an outer dewar containing a

superconducting solenoid maintained at 4.2 K. Inside this dewar was

another dewar of 4.5-inch bore. The inner dewar had a vacuum jacket

of copper around its lower portion only--the upper part was cooled

by the gas evaporating from both dewars. The superconducting magnet

around the inner dewar could be moved from the bottom to the top of the

apparatus during a run. The two dewars were separately filled with helium.

The inner dewar was pumped, maintaining a temperature of about 1 K.

Figure 1 shows the construction of the lower part of the apparatus

that was inserted into the inner dewar. The hot finger (a) in which

magnetic field probes could be inserted was of double wall construction

with superinsulation between the walls. This insert was introduced into

the apparatus through an O-ring seal into the pill vacuum line. The

cerium magnesium nitrate (CMN) pill (b) mounted inside the chromium

potassium alum (CrKalum) guard (c) on graphite posts (d) consisted

of a slurry of 50 mesh CMN in glycerol. Thermal contact to the slurry

was provided by twenty-five 0.005-inch OFHC copper fins (e) with a total

surface area of about 2000 cm^2. A stalk (f) of about 5000, 0.0031-inch

insulated copper wires was made by potting the wires in Epibond 100A.[14]

Thermal contact between the wires and the fins was maintained by electroplating

a thick layer of copper on the end of the wires and then electroplating

the fins to the layer (g). The upper part (h) of the CrKalum

radiation shield was fabricated on a teflon mandrel from strips of 0.005-inch OFHC

copper laid lengthwise down the mandrel and from cotton gauze impregnated
with Epibond 121,[14] which was wound around the copper strips on the
mandrel. Greater detail of the construction techniques of the pumping
equipment and pill design is contained in Reference 13.

Cooling below 1 K was obtained by the simultaneous demagnetization
of the CrKalum and CMN from a field of 46 kOe. ^{4}He exchange gas was
used to cool the salt pill and to conduct the heat of magnetization to
the 1 K bath. Typically, the pill was kept in thermal contact with the
1 K bath for one hour, the exchange gas was pumped for one hour and a half
and the demagnetization took forty-five minutes. After demagnetization
the ^{60}CoCo thermometer on the copper stalk (j) indicated a temperature
of about 3.5 mK. The superconducting solenoid was then slowly raised
out of the helium bath to the top of the apparatus; after this it became
normal in about fifteen minutes. After raising the solenoid the
temperature of the stalk increased to about 4 mK and subsequently warmed
at about 0.7 mK/hr at 5 mK and about 2 mK/hr at 10 mK.

The apparatus was designed so that none of the materials used would
become superconducting at their operating temperatures. In the parts
operating to 1 K cadmium-bismuth eutectic or silver solder was used to
make joints. The pill assembly was made of copper, mylar, phenolic plastic,
and different types of epoxy. Copper-copper joints on the pill assembly
were made by plating the parts together. Most magnesium samples were
bonded to gold or copper foils by gold diffusion bonds. Gold was first
evaporated onto copper foils, or magnesium specimens, and a gold or gold-
coated copper foil was clamped to the specimen and the two heated together
for four to twenty-four hours in a hydrogen atmosphere at 400°C. For
tungsten specimens, used to test the apparatus, gold previously evaporated
on the specimen's surface was diffused into the metal by heating at 1200°C;

copper foil was then electroplated to the gold diffusion layer. The foils

were then plated to the copper stalk $\left[\text{(i), Figure 1} \right]$. Lithium samples

were attached by local melting of one end of a sample onto a copper

foil with a spot welder or, for one rather small specimen, by pressing

copper wires into the metal. The effectiveness of the diffusion bonds

was shown by the results for the critical field curve for tungsten and

also by the experiments in which two ^{60}Co thermometers were used

connected by a ⋀ specimen   and   two diffusion bonds. (Isolation

  magnesium

between the thermometer systems was achieved by shielding each counter

with about 30 cm of lead.)

The magnetic field on the specimen was made as small as possible

with three pairs of Helmholtz coils. Fields could be measured with a

magnetometer[15] or a rotating coil gaussmeter probe[16] and

lock-in amplifier. With the apparatus out of the dewar but with the dewars

at liquid nitrogen temperature the field at the specimen site was adjusted

to 0 ± 2 mOe and the field gradients, $\partial H_x/\partial x$, etc., to 0 ± 1 mOe/cm.

The axial field profile was also measured. The apparatus was then replaced

in the dewar. With no specimen or copper stalk on the pill the field

probes could be placed at the specimen position; with a specimen, the

field probes were placed just outside the measuring coils. With the

probes in the specimen position it was found that after demagnetization

from 46 kOe, raising the magnet and allowing it to go normal, there was

a residual axial field at the sample site of between 10 mOe and 20 mOe.

This field, caused by the magnetization of the surrounding laboratory,

returned to zero within about a week. In an experiment with a sample

in position the field on the sample could be estimated from the field

measured some distance away during the experiment and from the field

profile measured before the experiment. During an experiment the axial

field was swept with a solenoid wound over the mutual inductance coils.

The transverse field was also systematically changed by varying the currents in the Helmholtz coils. Superimposed on the static residual field was an 8 mOe pulsed field from the Bevatron with a 6 second period. The estimated field on a sample during an experiment was 0 ± 0.01 Oe.

The onset of superconductivity was detected by the change in susceptibility of the sample, which was measured with a 17-Hz commercial version[17] of the mutual inductance bridge designed by Pillinger et al.[18] The sensitivity of this bridge was improved by using a lock-in amplifier and by replacing the bridge amplifier by a lower noise operational amplifier. The mutual inductance coils, [(k), Figure 1] had compensated primaries and 50,000 turns of 0.0063-inch copper wire on each of two secondaries. The secondary circuit was series tuned with 2.2 μF of capacitance. The usual method of operation was to change the field on the sample by sweeping the current in a solenoid wound over the mutual inductance coils.

The mutual inductance system was sufficiently sensitive that at 5 mK the transition of a sample of 1/8-inch diameter tungsten rod of resistivity ratio 17,000 was observed with a signal to noise ratio of 50 (time constant three seconds) when the primary current in the mutual inductance coils produced an rms field of 3 mOe. The volumes of the lithium and magnesium samples used were larger than the tungsten by a factor of two to five. The resistivity ratios of the samples after mounting was not known, but the mounting procedure used strained the samples so that a resistivity ratio comparable with that of the tungsten was unlikely. Thus, even for comparable size specimens, the signal to noise ratio should have been greater than 50. Experiments on a sample of magnesium with a second thermometer mounted above the sample showed that there was no detectable difference in temperature between the two thermometers with the bridge primary field increased to 60 mOe rms,

Nuclear orientation thermometry

Temperatures were measured using a nuclear orientation thermometer.
A single crystal of hexagonal cobalt was cut into needles with the axis
of the needles parallel to the c-axis. The needles were irradiated
with neutrons to produce ^{60}Co _in situ_. For a good single crystal the
large anisotropy field of 5 kOe and the small demagnetizing factor
ensure that closure domains are small and most of the Co atoms are in
domains magnetized along the c-axis, subjecting all the nuclei to the
same hyperfine interaction. The ^{60}Co nuclei are thermally distributed
among the magnetic sublevels of the ground state split by the hyperfine
interaction. Gamma rays emitted from states in ^{60}Ni fed from the ^{60}Co
ground state have an anisotropic distribution; the anisotropy depends
on the extent of the polarization of the ^{60}Co nuclei, the nature of the
gamma transitions and depolarizing effects of intermediate transitions.

The angular distribution of the gamma rays normalized to unity
at high temperature is given by[19]

$$W(\theta , T) = 1 + U_2 F_2 Q_2 B_2(T) P_2(\cos \theta)$$

$$+ U_4 F_4 Q_4 B_4(T) P_4(\cos \theta)$$

with $U_2 F_2 = -\frac{2}{7} \sqrt{\frac{13}{6}}$ and $U_4 F_4 = -\frac{\sqrt{26}}{21}$ for ^{60}Co

Here Q_2 and Q_4 are solid angle corrections dependent on the experimental
geometry. For this experiment $Q_2 = .996$ and $Q_4 = .985$[20,21]. These
corrections differ only slightly from unity because our 3 in. x 3 in.
Na(Tl) detectors were located 24 in. from the thermometer. The P_2 and P_4
functions are Legendre polynomials. The statistical tensors

$$B_k \equiv (2I + 1)^{\frac{1}{2}} \sum_{M=-I}^{I} (-1)^M (IMI\text{-}M \mid IIk0) \, \rho_{MM}(T)$$

contain all the temperature dependence. The diagonal elements of the

density matrix ρ_{MM} are evaluated from the spin-Hamiltonian for the

parent ground state.

In assessing the merits of a thermometer for use at very low

temperatures several factors must be considered: freedom from systematic

errors, precision, useful temperature range, heating effects, presence

or absence of fields, the time required to make a measurement and the

experimental complexity of the measuring system. These factors are

briefly discussed below with particular reference to ^{60}Co Co.

In principle the temperature derived from an orientation thermometer

is very reliable as it comes from the Boltzmann distribution of nuclei

in the parent ground state. However, the properties of the parent

ground state and its modes of decay must be known. In the case of ^{60}Co Co

the decay scheme is particularly simple. The ^{60}Co ground state has a

half life of 5.3 yrs, I = 5+ and the splittings are well described by a

hyperfine field of 227 kOe parallel to the c-axis[22]. The spin-lattice

relaxation time has been measured using magnetic resonance and shown to

be temperature independent at about 75 sec below 14 mK[23]. Temperatures

were determined from the anisotropy of the 1.17 MeV and 1.33 MeV

gamma rays emitted in the decay of ^{60}Co to ^{60}Ni[24]. The observed gamma

rays, the 4+(E2)2+(E2)0+ cascade, are fed from the ^{60}Co ground state by a

L=1, beta-transition to the ^{60}Ni 4+ state. Only about 1 in 10^4 of the

2+(E2)0+ transitions are fed by another decay. Since the transition is

"stretched"[25,26] the anisotropies of the two gamma rays are the same. Several

values of W(θ = 0 , T) are given in Table II for ^{60}Co Co.

The accuracy of a temperature measurement is influenced by the value of $\partial W(\theta, T)/\partial T$, by statistical counting errors and by systematic errors. The time required for a measurement varies with the desired accuracy and the tolerable rate of radioactive heating. For a counting rate of 6000/min, which can be obtained with a heating rate of 0.1 erg/min, a value of $W(\theta, T)$ can be determined to ± 10 percent in 1 sec and ± 1 percent in 100 sec. It should be noted that most systematic errors tend to give too low an anisotropy; that is, the apparent temperature is too high.

To make measurements with single-crystal hcp cobalt, no electromagnetic fields are required. Since the gamma rays are very penetrating, the detectors can be outside the apparatus. A concomitant disadvantage is that it is difficult to use two thermometers with the same emitting nucleus in close proximity to each other. We have used two ^{60}Co thermometers separated by a few inches by installing lead collimators leading to separate detectors. There is no difficulty in using two thermometers with nuclei emitting gamma-rays at different energies; we have used a ^{60}Co single crystal thermometer and also a ^{54}Mn Fe foil, with polarizing field, in the same apparatus.

The main difficulties in using a gamma ray thermometer are associated with the effects of radioactive heating. (For those thermometers in which the daughter nucleus is formed by electron capture or in which an isomeric state is used, this does not apply.) We used a source giving a high-temperature counting rate of 8000/min for each 3 in. x 3 in. Na(Tl) detector 24 in. from the source. This introduced heat at 2 erg/min into the thermometer; in other applications with counters closer to a weaker source heating of 0.1 erg/min could be obtained for the same counting rate. For a crystal of thickness d and cross-section A, $d << \sqrt{A}$, the thermal relaxation time of the crystal is $C_v d^2/k\pi^2$, where C_v is the volume

specific heat and k the thermal conductivity. Assuming C_v is a Schottky anomaly due to the splitting of the [59]Co ground state, $k = T$ watt/K-cm , and $d = 1mm$ the thermal relaxation time has a maximum value of about 0.1 sec.

Thermal contact between an orientation thermometer and the surroundings must be sufficiently good that the temperature rise due to radioactive heating is small. If a soft-soldered joint is used in making contact, it has been found that for self-heating of 10^{-2} erg/sec and a contact area of $1cm^2$ at 10mK a temperature difference of order 1mK is to be expected[27,28]. For a metallic joint in which heat is conducted by electrons, such as through a screwed contact[27] or a soft-soldered joint in which trapped flux keeps the solder normal[27], a temperature difference or order 10^{-4} mK might be expected. In our experiments the thermometer was electroplated with copper to the stalk. We observed that the lowest temperature reached by the apparatus did not change when the heat current density from the thermometer changed by a factor twenty. This suggests that for this method of joining, thermal contact is adequate.

If an orientation thermometer is used in liquid helium,as in a dilution refrigerator, the contact to the helium is relatively poor. For example, if we again assume a heat load of 10^{-2} erg/sec, a contact area of $1cm^2$, a boundary resistance of $10^{-5} / (AT^3)$ K-sec/erg[29], we find at 10mK, $\Delta T = 100mK$! Thus the thermometer should be attached, using copper plating or a screwed contact, to a large surface area (such as sintered copper[t]) in contact with the helium. For a dilution refrigerator the thermometer should not be attached to the walls of the mixing chamber as they may be hot through heat leaks to the chamber[30].

To determine the anisotropy of the ^{60}Co gamma rays it is only necessary to count the number of gamma rays in a window including the two gamma photopeaks. If a polar and an equatorial counter are used, a direct measurement of anisotropy is made. If only a polar counter is used, measurements must be taken with the thermometer cold and these must be normalized to counts taken with the thermometer sufficiently warm that there is no anisotropy. The latter option was our normal operating procedure, with the addition of a final series of warm counts after the run. Care must be taken to ensure that the quantities of liquid helium and nitrogen between the thermometer and the counter remains constant during the run or the attenuation of the gamma rays will be slightly changed.

We have checked for complete saturation of the magnetization of the single crystal ^{60}Co thermometer. We compared the measured temperature with and without an external polarizing field and found that for the thermometer used in the experiments there was agreement to within the experimental error of 5 percent. The accuracy was limited by drifts in temperature due to applying the polarizing field.

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† We have used commercial sintered copper in heat exchangers for dilution refrigerators, in particular Grade H OFHC from Pall Trinity Micro Corp and Feltmetal from Huyck Metals.

RESULTS

In order to check that the apparatus was working properly, the
critical field curve of a sample of 99.999% tungsten[31] was measured.
As described above, the tungsten was attached to the copper stalk by
plating copper onto a surface of gold partially diffused into the bulk material.
The resistivity ratio (4-300 K) of the sample after diffusion bonding
and plating was 17,000. In addition to the transition near 15 mK, a
transition was also observed near 2K. A sample which had not been
subjected to the gold evaporation, heating and bonding process did not
show this high-temperature transition. We attribute this transition to the
presence of small amounts of β-tungsten formed during the bonding process
which becomes superconducting in that region.[32,33] The critical field curve
measured in two experiments on tungsten to 5 mK gave values of H_c
about 10% different from those of Black et. al.[12] Furthermore,
some hysteresis was observed on changing the polarity of the applied
field. We think this was due to the presence of trapped flux in the
β-phase. We also found that the transition occurred in a time not
exceeding five seconds; occasionally superheating was observed when the
transition occurred faster than the response time of the bridge. This
may be compared with transition times of several minutes obtained by
Black et al. In their experiment thermal contact was limited by the
Kapitza boundary resistance between the sample and the ^{3}He used as a
thermal contact agent. We found no difficulty in following the transition
to a temperature corresponding to a critical field of about one-tenth of
that at T = 0. These results show that thermal contact between pill,
sample, and thermometer was adequate.

Data for the different samples of magnesium and lithium are given

in Table III. We were unable to find a superconducting transition in

any of the samples. This does not completely rule out the possibility

that T_c is greater than 4 mK, because the samples may have supercooled.

For pure, unstrained materials with a transition temperature in the

millikelvin range, the coherence length ξ at $T = 0$ is very long,

giving a small Ginsberg-Landau κ and type I superconductivity.

At a temperature at which the thermodynamic critical field is H_c the

lowest field to which the sample can remain normal is $H_{c3} = 2.4\,\kappa\,H_c$

for surface nucleation, and $H_{c2} = \sqrt{2}\,\kappa H_c$ for bulk nucleation.

In Table IV estimates of H_{c2}, H_{c3}, ξ, and κ are given in the clean

and dirty limits. Nucleation of the transition above H_{c2} or H_{c3}

can occur if nucleation centers exist and are effective. Faber and

Pippard[34] have shown that in aluminum and tin the criterion for a flaw

of size δ to be effective is $\delta > > \xi$. In experiments on aluminum they

estimated that flaws of $10^{-3} - 10^{-4}$ cm existed in their specimens. These

experiments were made in the middle of carefully made rods of material

as nucleation appeared to start at the ends of the rods or at other

surface irregularities. This is the usual situation for superconductors

with critical temperatures of 1 K or higher--special care is usually

necessary to observe appreciable supercooling. For low T_c superconductors

it may be more difficult to achieve nucleation since ξ is larger. However,

in their experiments on tungsten, Black et al.[12] found that nucleation

occurred at about $0.2\,H_c$ unless the surface had been specially prepared;

we also found that tungsten did not supercool below $0.2\,H_c$.

Our magnesium samples were far from homogeneous; parts of the surface

were covered with a gold diffusion layer and the clamps used during the

diffusion bonding process produced varied strains in the crystals.

The lithium samples self-annealed at room temperature after the mounting

process but the martensitic transformation severely strained the crystal

each time it was cooled. Therefore, it is clear that our lithium and

magnesium samples were strained to a greater degree than the tungsten

sample. Nevertheless, if T_c is lower than for tungsten, ξ might

be longer and it could be more difficult to achieve nucleation in spite

of the less perfect state of the samples. Since the mechanism by which

defects act as nucleation centers is not understood in detail, it is

not possible to predict with any degree of certainty the supercooling

behavior of the lithium and magnesium samples from that of tungsten

and higher T_c superconductors. However, as a rough guess, it seems

probable that a transition would have been observed if T_c were as

high as 6 mK. For T_c = 6 mK, H_c(4 mK) ≈ 0.15 Oe, and between 4 mK

and 5 mK the samples would, at some time, have been in a field that

was only 4% of H_c. Furthermore, at 4 mK ξ would have a value

comparable to its 0 K value.

CONCLUSION

We have cooled lithium and magnesium to 4 mK in magnetic fields

of 10^{-2} Oe and to 5 mK at 5×10^{-3} Oe without observing superconducting

transitions. The possibility that the samples supercooled precludes

setting a definite upper limit to T_c, but it seems probable that

$T_c \lesssim 6$ mK. At best, we have explored 60% of the temperature range

predicted for T_c for magnesium; for lithium the theoretical estimates

of T_c are so much in doubt that we may still be far from the region

of the transition.

Table I.   Comparison of theoretical and

empirical values of λ.[a]

	Be	Mg	Zn	Cd
Value of λ calculated by Allen and Cohen.	0.26	0.31	0.42	0.40
Value of λ derived from heat capacity enhancement.	0.25	0.33	0.43	0.36
Value of λ derived from Eq. (4).	0.23	--	0.38	0.38

[a] See reference 1.

Table II. Values of W(0 , T) for ^{60}Co in Co

thermometer (with $Q_2 = Q_4 = 1$)

T(mk)	$B_2(T)$	$B_4(T)$	W(0 , T)
1.0	1.6964	1.1721	0.00197
1.5	1.6823	1.1399	0.01574
2.0	1.6517	1.0727	0.04491
2.5	1.6086	.9831	0.08478
3.0	1.5574	.8846	0.1303
3.5	1.5015	.7861	0.1777
4.0	1.4430	.6928	0.2249
4.5	1.3837	.6075	0.2706
5.0	1.3244	.5314	0.3141
5.5	1.2658	.4630	0.3552
6.0	1.2085	.4036	0.3938
6.5	1.1528	.3519	0.4297
7.0	1.0989	.3069	0.4633
8.0	0.9970	.2343	0.5238
9.0	0.9037	.1802	0.5762
10.0	0.8191	.1396	0.6216
12.0	0.6745	.0861	0.6954
14.0	0.5591	.0551	0.7515
16.0	0.4670	.0364	0.7948
18.0	0.3939	.0248	0.8283
20.0	0.3352	.0174	0.8548
25.0	0.2329	.0080	0.9002
30.0	0.1695	.0041	0.9277

Table II. (Continued)

T(mk)	$B_2(T)$	$B_4(T)$	W(0 , T)
35.0	0.1283	.0023	0.9455
40.0	0.1002	.0014	0.9575
45.0	0.0803	.0009	0.9660
50.0	0.0657	.0006	0.9722
100.0	0.0168	.00004	0.9928

Table III. Samples.

	Supplier	Purity	Initial Resistivity Ratio	Bonding Method
Li I	Bram Metallurgical	99.9+%	825	Local welding.
Li II	P. H. Schmidt [d]	99.9998%	4×10^3	Metal-metal pressure contact.
Mg I	R. A. Stark [e]		$\sim 10^6$ [b]	Gold diffusion bond.
Mg II	Research Organic/ Inorganic Chemical Corporation	99.99%	330 [a]	Local welding.
Mg III	R. A. Stark		$\sim 10^6$ [b]	Gold diffusion bond.
W	Semi-Elements	99.999%	5.7×10^4 [a,c]	Gold diffusion bond-Cu plate.

[a] Resistivity ratios determined by the authors by potentiometric and eddy current techniques agreed to within 20% on the samples of tungsten and magnesium.

[b] Mean free path of similar samples grown by the author were $\sim$ 15 cm.

[c] This resistivity ratio was measured on a different sample, from the same supplier, from the one used in the experiment.

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Table IV. Superconductive Parameters for Li, Be, W, and Mg.

	Li	Be	W	Mg	Unit
T_c, superconductive transition temperature (measured)		0.026	0.0154		K
(assumed)	0.004			0.004	
ρ_{300}, resistivity at room temperature	9.4	3.6	5.3	4.3	$\mu\Omega$-cm
γ, electronic specific heat coefficient.	1250	470	1056[a]	930	erg/°K^{-2}cm^{-3}
γ/γ_o	2.2	0.428	0.663	1.33	
H_c, thermodynamic critical field at 0 K.	0.355	1.3	1.15	0.306	Oe
S/S_o, ratio of Fermi surface area to FEM area.	0.787[b]	0.65[b]	0.111[c]	0.60[d]	
$v_F = h/m(3\pi n)^{1/3}$ = Fermi velocity in FEM	1.285×10^8	2.25×10^8	2.20×10^8	1.58×10^8	cm/sec
$v_F^* = (\gamma_o S/\gamma S_o)v_F$ = renormalized Fermi velocity.	0.46×10^8	3.42×10^8	0.369×10^8	0.713×10^8	cm/sec
$\xi_o^* = 0.18(h v_F^*/k_B T_c)$, renormalized coherence distance	0.0158	0.0181	0.0032	0.0245	cm
$\lambda_L^*(0) = (\pi/\gamma)^{1/2} c k_B/2 e v_F^*$, renormalized penetration depth	4.69×10^{-6}	1.03×10^{-6}	6.36×10^{-6}	3.52×10^{-6}	cm

Table IV. (Continued)

	Li	Be	W	Mg	Unit
$\kappa_c^* = 0.96\ \lambda_L^*(0)/\xi_o^*$, renormalized GL parameter in clean limit	2.87×10^{-4}	0.55×10^{-4}	1.92×10^{-3}	1.38×10^{-4}	
$\kappa_d = 0.75\ \lambda_L^*(0)/\ell = 7.9\times10^{-3}\ \rho_r^{1/2}$ (ρ in $\mu\Omega$ cm GL parameter in dirty limit[e])	0.0263	0.00617	0.0136	0.0103	
H_{c3} clean $= 2.4\ \kappa_c^* H_c$	2.45×10^{-4}	1.75×10^{-4}	5.30×10^{-3}	1.01×10^{-4}	Oe
H_{c3} dirty[e] $= 2.4\ \kappa_d H_c$	0.022	0.019	0.037	0.0076	Oe

[a] From specific heat measurements on a sample similar to that used in these experiments (to be published).

[b] Estimated from the reduced resistivities--see J. M. Ziman, Electrons and Phonons p. 374.

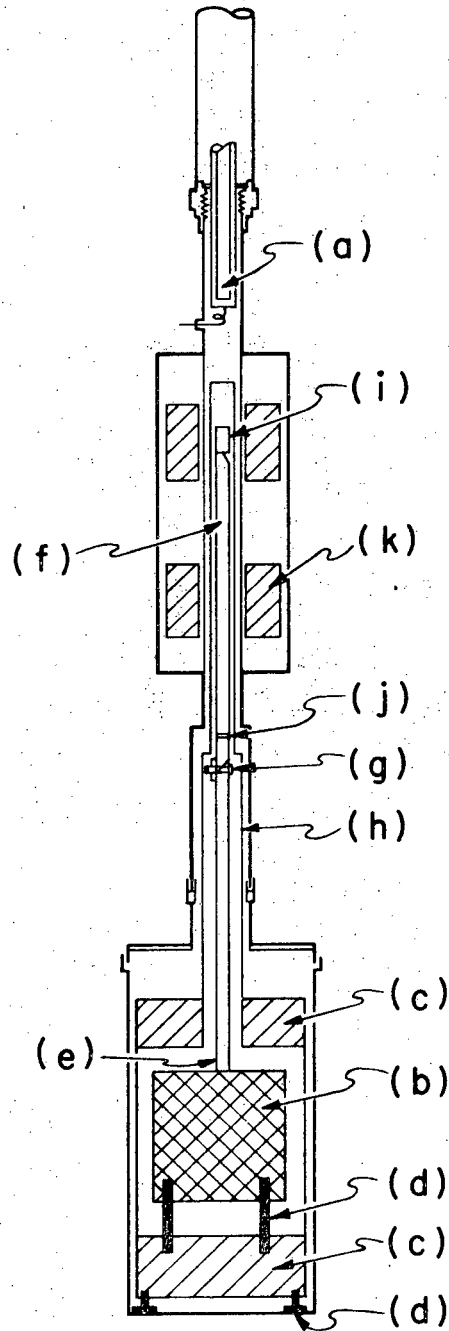[c] E. Fawcett and D. Griffiths, J. Phys. Chem. Solids 23, 1631 (1962).

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[e] Resistivity ratio of 100 assumed.

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XBL706-3185

Fig. 1. Detail of lower section of apparatus.

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