Thermal Contact to Lithium Metal

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Abstract

Experiments at ultra-low temperatures require very low thermal contact resistances, a serious issue even for metallic specimens below 1 mK. Customary practices include pressed contacts or welding by some means, *e.g.* diffusion welding. When dissimilar metals are joined, one must avoid excess formation of an alloy, usually a poor thermal conductor. The most firm contact with possibly deep alloying does not always have the best thermal conductivity. We have studied this problem when pressing lithium metal to contact with copper, silver and gold. The results are surprisingly different - good contacts could be produced only between Li and Cu, not with Li and Ag or Au. This is obviously due to easy alloying of Ag and Au with Li even at room temperature. This information is essential for proper materials choice in our planned experiment on superconductivity and nuclear magnetism on lithium metal.

Key words: lithium metal; thermal contact; nuclear magnetism; superconductivity

There is interest for experiments on lithium metal at very low temperatures due to the quest for its anticipated superconductivity at millikelvin regime [1]. Another motive for studying Li is nuclear magnetism. Natural lithium contains 93 % of the isotope ^{7}Li, which has a nuclear magnetic moment $\mu = 3.256\ \mu_N$, larger than that of copper. Spontaneous nuclear magnetic ordering is expected at nanokelvin range. Such low nuclear spin temperatures can be produced by cascade nuclear demagnetization cooling [2]. By simple arguments the Li nuclei should order ferromagnetically, which would strongly influence the weak superconductivity. Mutual interplay of superconductivity and nuclear magnetism has been studied in some metals but so far in the regime of weak interference only [3].

Our nuclear demagnetization refrigerator can cool metallic specimens clearly below 100 μK, and by performing second adiabatic demagnetization for the sample itself, record low nuclear spin temperatures have been produced [4]. At such low temperatures the thermal contact between the sample and the refrigerant or precooling stage is of decisive importance.

Producing highly conducting interface between two dissimilar metals is not trivial. Good results have been reported by the use of electron-beam welding or diffusion welding, which are applicable for wide variety of material combinations [5]. By these methods the poorly conducting mixed region is very thin and in control to some extent by choosing proper process parameters. The work on lithium is complicated by its high reactivity and necessity for hermetic sealing.

The capsuling metal must not be magnetic nor superconducting itself. Obvious, and practically sole, group of candidates is the noble metals copper, silver, and gold. The sample and its protecting cover must be thin, of the order of 10 μm, to avoid eddy current screening in the planned NMR measurements. We chose to study a series of test samples flattened by squeezing in between two cover foils. The diffusion joint was produced by heating up the clamping system together with the foils up to the desired temperature and re-tightening the holding screws by an adjusted torque. Direct electrical contact between the capsuling foils was prevented by a kapton sheet, 25 μm thick and pierced at the center for placing the sample. The foil assembly was finally sealed by Stycast epoxy (1266 or

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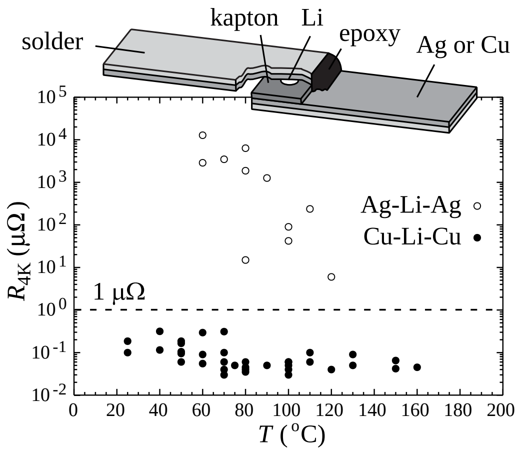

Fig. 1. Contact resistances as the function of the diffusion welding temperature; the sample geometry at the top.

2850 FT). All this was done in a glove box in argon atmosphere with less than 10 ppm oxygen.

To measure the contact resistance, the capsuling foils were first covered on one side by ordinary soft solder, superconducting at 4 K. This way the voltage taps of the 4-wire measurement could be placed at any distance − only the thin normal metal-lithium-normal metal sandwich contributed to the resistance. The solder coating could be thinned to $\sim 50\ \mu$m; the foils were carefully cleaned prior to the work in the glove box.

When flattened between the cover foils the lithium spots became about 3 mm in diameter with a thickness of the order of 50 μm. A set of samples were welded to silver and copper foils, in most cases 50 μm thick. Lithium was obtained from two different suppliers with analyzed purity better than 99.9% [6]. The residual resistivity ratio was 900 ± 100, while those of Cu and Ag (99.9%) were about 300 and 70, respectively. No attempt was made to improve the bulk conductivities.

Fig. 1 shows some measured contact resistances of Li to Ag and Cu. The welding pressure was varied between about 60 . . . 120 MPa and the indicated temperature was sustained for 1 to 15 min. From Fig. 1 it is clear that the most essential factor was just the chosen capsuling metal: all silver data are above 1 $\mu\Omega$, which we set as somewhat arbitrary limit for good contact, while copper capsules always produced results better than this, irrespective of the diffusion welding parameters. The scatter for the silver capsules is huge suggesting an uncontrolled factor influencing the process. There is no data for silver capsules above 120 °C because Li was then found to completely penetrate through the silver foil producing a dark spot on its surface. This suggests that Li mixes eagerly with silver, rapidly at elevated temperatures but appreciably already at room temperature, and that the poor results are due to formation of Li-Ag alloy at the contact. More test joints were made using 25 μm silver foil. The results have the same characteristics, but the seeming temperature dependence of Fig. 1 for Ag is more or less washed out.

The deteriorating effect of silver and the applicability of gold was checked by making multiply layered joints, where a copper capsule was used to conceal a small copper, silver, or gold foil with lithium spots on both sides. $R_{4\mathrm{K}}$ was again small when Li was in contact with Cu only, but when there was Ag in the package, the result was as poor as for the silver capsules. Also gold resulted in large resistances and is thus not suitable as sealing material. The dramatically different effect of copper and silver can be understood by examining the phase diagrams of the Li-Ag and Li-Cu systems [7]. Ag in Li has a lithium rich eutectic phase with a lower melting temperature than that of pure Li, while there is no such phase for Cu in Li. No systematic data is available for Li-Au but obviously it behaves as Li-Ag. A remark upon alloying of lithium and gold under pressure in Ref [8] is in accordance with our results.

Some samples were stressed deliberately by repetitive thermal cycling. No change in $R_{4\mathrm{K}}$ was observed, although some dilapidation might have been expected due to differential thermal contraction and/or the martensitic phase transition of Li at about 80 K [9].

In conclusion, we can not use silver or gold for capsuling lithium for our low temperature experiments due to mixing of the metals already at room temperature. On the contrary copper suits well for such purpose. Good diffusion welding results were obtained with > 100 MPa for 10 min above 80 °C. Typical contact resistances were of the order of 0.2 $\mu\Omega\mathrm{mm}^2$.

References

[1] T.L. Thorp et al., J. Low Temp Phys **3** (1970) 589; K.M. Lang et al., ibid. **114** (1999) 445; J.K. Freericks et al., Physica B **284-288** (2000) 425; N.E. Christensen et al., Phys. Rev. Lett. **86** (2001) 1861.

[2] A.S. Oja et al., Rev. Mod. Phys. **69** (1997) 1; J.T. Tuoriniemi et al., Physica B **280** (2000) 474.

[3] S. Rehmann et al., Phys. Rev. Lett. **78** (1997) 1122; T.A. Knuuttila et al., ibid. **85** (2000) 2573; M. Seibold et al., J. Low Temp. Phys. **110** (1998) 363; T. Herrmannsdörfer et al., ibid. **124** (2001) 257.

[4] W. Yao et al., J. Low Temp. Phys. **120** (2000) 121; T.A. Knuuttila et al., ibid. **123** (2001) 65.

[5] Yu.M. Bunkov, Cryogenics **29** (1989) 938; S. Yin et al., Rev. Sci. Instrum. **62** (1991) 1370.

[6] Alfa Aaesar, Johnson Matthey GmbH, Karlsruhe, Germany; ABCR GmbH, Karlsruhe, Germany.

[7] M. Hansen, *Constitution of binary alloys* (McGraw-Hill, New York, 1958).

[8] T.H. Lin et al., Phys. Rev. B **33** (1986) 807.

[9] A.Y. Liu et al., Phys. Rev. B **59** (1999) 4028; Refs therein.