Martensitic transformation of lithium: Magnetic susceptibility measurements

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The magnetic susceptibility of lithium has been measured at 78 K both before and after cooling to 4 K to initiate the martensitic phase transformation. The susceptibility increases on the initial transformation by 7–26 %, but this becomes systematically less for successive transformation cycles until no effect of cycling can be seen, in disagreement with previous bulk measurements. The magnetic change reverts rapidly up to about 120 K but then shows a prominent tail up to about 170 K, which may be due to the fcc phase during the reversion. A large residual-resistance annealing peak has been observed between 110 and 160 K, which correlates with the phase reversion. [S0163-1829(97)01338-6]

A martensitic transformation from bcc to a highly faulted close-packed phase was discovered in lithium by the x-ray experiments of Barrett;[1,2] the transformation has a large temperature hysteresis between its onset on cooling (at M_s) and the final reversion on warming, ≈ 70–170 K. Subsequent experiments on specific heat,[3,4] elastic properties,[5] and in particular the electrical resistivity,[6–8] soon confirmed the x-ray work. The resistive behavior of lithium is complicated because the Fermi surface and the phonon properties are both altered by the phase transformation, and also because of conversion between the several close-packed phases, but the evidence showed that the extent of the transformation was little affected by thermal cycling.[3,7] Magnetic susceptibility is a simpler measure of phase transformation than resistivity since the large phonon temperature dependence is absent. Confirmation of changes in the electronic properties of lithium came from susceptibility experiments by Hedgcock,[9] and Lueken;[10] however, in neither of these papers was the reversion to the bcc phase studied, or the effect of multiple cycles, which are the main subjects of this paper.

Further work has shown that the initial low-temperature phase is of the $9R$ type.[11] Recent neutron-scattering experiments (cf. Refs. 12–16) have produced more details about the structures of the faulted close-packed phases. In particular that (a) the $9R$ phase is often accompanied by a large and variable amount of ''disordered polytype'' (i.e., the simultaneous presence of fcc, hcp, and $9R$ on a length scale of a few lattice spacings), and (b) the $9R$ and polytype phases can order between ≈ 80 and 120 K to form an fcc phase which is stable above ≈ 80 K, but which reverts to bcc between ≈ 140 and 180 K.[12]

The polycrystalline samples used in the present work came from the same source as in the resistivity work.[6–8] Their residual resistivity indicated that the amount of impurity in solid solution was ≈ 0.02 at. %, but more significant is the amount of ferromagnetic impurity. The samples discussed below showed *no* nonlinearity of magnetization, *no* hysteresis, and *no* remanence. These effects were seen in a few early samples (equivalent in the largest case to ≈ 2 ppm of iron), but measurements showed that the contamination made no significant difference to the changes caused by phase transformation. The balance precision was $\approx 0.5\%$ for

a sample of mass typically 0.1 gm, and individual susceptibility values have an absolute uncertainty of $\pm 2\%$.

The change of susceptibility was studied by progressively warming through the reversion region samples which had been cooled to 4 K, and measuring their moment after re-cooling to 78 K. The results of four successive cycles on sample 1 are shown in Fig. 1, where the susceptibility ratio is normalized to the fully reverted bcc phase. The disappearance of the effect of transformation was unexpected, but several other samples all showed qualitatively similar behavior, as summarized in Table I.

The *first* reversion cycles for all the samples are shown in Fig. 2, and the full results are discussed below.

(i) The mean value for the magnetic susceptibility of bcc lithium at 78 K from the 15 sets of data in Table I is 24.5 ± 0.3 (10^{-6} cm^3 mole^{-1}), which is in good agreement with the reported values at 298 K of 24.9± 0.3 (Ref. 9) and 23.9
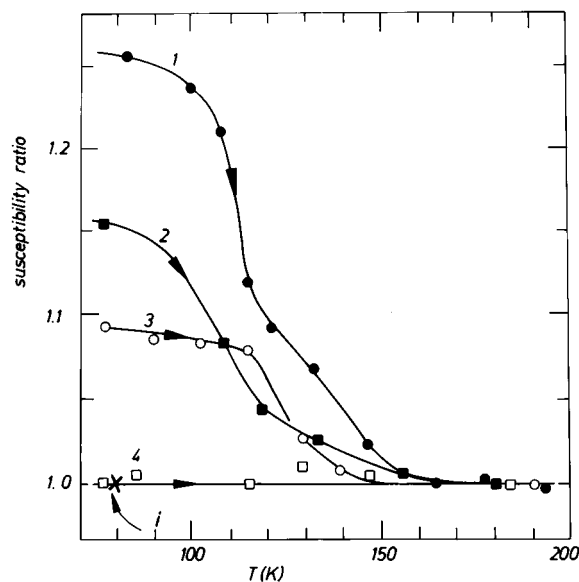

FIG. 1. The effect of four successive temperature cycles on the susceptibility ratio (see text) of lithium at 78 K. Curves 1–4 show the changes after sample 1 was cooled to 4.2 K, then heated to the temperature shown for ≈ 10 min, and then remeasured at 78 K. The initial value on cooling the bcc sample from ≈ 200 K is shown by **i**.

TABLE I. The decrease of susceptibility ratio (see text) for lithium with successive temperature cycles through the transformation region.

	Susceptibility ratio for sample				
Cycle	1	2	3	4	5
First	1.26	1.07	1.09	1.14	1.10
Second	1.16	1.05	1.00	1.02	1.05
Third	1.08	1.04			1.04
Fourth	1.00	1.01			

± 0.6 (Ref. 10) (10^{-6} cm^3 mole^{-1}) and with the *increase* of ≈ 0.3 (10^{-6} cm^3 mole^{-1}) expected on cooling bcc lithium from 298 to 78 K.

(ii) The initial ratio in Table I varies from 1.07 to 1.26 as a result of the production of the close-packed phase (cf. the values of 1.06 and 1.14 from Refs. 9 and 10), so that the susceptibility (and the density of states of conduction electrons) in the close-packed phase(s) of lithium must be *at least* 26% greater than for the bcc phase. There are no explicit calculations of the susceptibilities of the $9R$, fcc, or hcp phases of lithium, but calculations of the density of states at the Fermi surface (cf. Fig. 6 of Ref. 14), suggest that it is similar in value for all the close-packed phases, and $\approx 10\%$ larger than for the bcc phase, i.e., less than half as much as shown by the present results (cf. also next paragraph).

The fourfold variation of the initial increase shown by Table I is barely consistent with the variation reported by the neutron work for the *amount* of the low-temperature phase, (cf. Refs. 13 and 15), and this suggests that the variation of susceptibility is due to different proportions of the $9R$ and polytype phases having significantly different susceptibility.
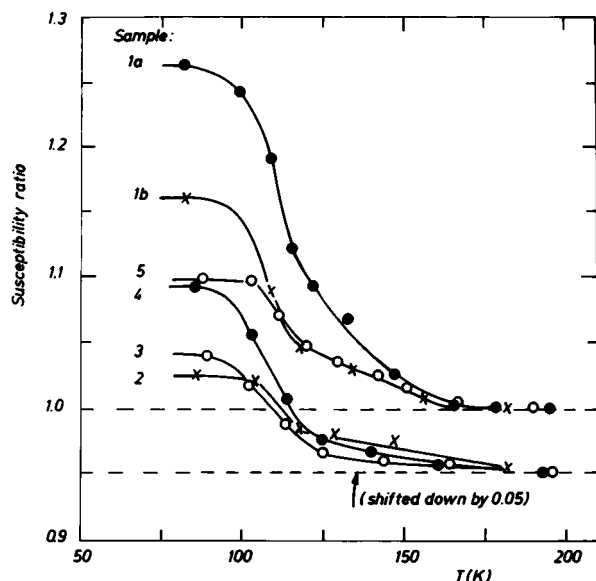

FIG. 2. The susceptibility ratio (see text) for lithium during the first reversion cycle. Curves 1–5 correspond to the samples of Table I; 1a is for the first cycle of reversion, 1b is for the second cycle (curves 2, 3, and 4 are offset by 0.05 for clarity). The sequence of measurement is as in Fig. 1.

Support for this idea comes from the anomalous curvature in the change of resistivity of two-phase lithium with hydrostatic pressure,[8] which is evidence that *reversible* changes of composition of $\approx 5\%$/kbar are occurring between coexisting phases with significant differences in their electrical properties, and perhaps also their magnetic ones.

The largest amounts of phase transformation were expected on the first cooling of well-annealed samples, but the large increase for sample 1 occurred after several previous cycles between ≈ 64 and 300 K (these were not studied in detail before the results shown in Fig. 1). Samples 2 and 3 in the table were virgin samples on first cooling to 4.2 K; sample 4 was the same as sample 3 but remeasured immediately after slow warming up to ≈ 300 K, and sample 5 was the same as sample 1 but remeasured after several weeks at ≈ 300 K. None of these later samples, however, gave as large a change as sample 1. It is commonly believed that the large residual stresses after transformation reduce the amount of a subsequent transformation (cf. below); however, the present data show the facts are less simple, since samples where there is considerable residual stress distribution (e.g., 1 and 4) can nevertheless show large amounts of transformation.

(iii) The systematic decrease of susceptibility with cycling shown in Fig. 1 is presumably due to progressive inhibition of the transformation. An almost complete inhibition is well known in *sodium*, but it has not hitherto been reported in lithium; in fact, there is strong counter evidence from magnetoresistance work on polycrystalline samples where multiple cycles did *not* significantly affect the amount of phase transformation.[7] The Fermi surface of bcc lithium is appreciably distorted from a sphere, and as the distortion is sensitive to the proximity of the Brillouin-zone boundaries, the shape of the Fermi surface and the galvanomagnetic properties of lithium change considerably on phase transformation. The magnetoresistance of lithium falls threefold on transformation, but its value at 4.2 K varies very little with repeated reversion cycles, and plastic deformation at 4.2 K produces only a few percent increase in its value.[7] These facts indicate that the amount of low-temperature phase formed on cooling must be more than $\approx 70\%$, that the amount varies little on cycling, and that the different low-temperature phases must all have similar magnetoresistance. The magnetoresistance and the susceptibility samples were made from the same stock of lithium, and while no structural measurements were made, the changes are clearly due to the martensitic transformation in both cases. Differences arising from the sample form also appear unlikely since neutron work shows that polycrystalline wires of diameter ≈ 1 mm (typical of both experiments) behave without significant difference from large single crystals.[15] The conclusions from susceptibility and from magnetoresistance both appear to be strong, but mutually inconsistent: this is a puzzling anomaly.

(iv) The shape of the reversion curves shown in Fig. 2 is similar for all samples, with onset at ≈ 90 K followed by a rapid decrease to ≈ 120 K and succeeded by a slower reversion tail ending at ≈ 170 K. These curves are similar to those obtained by integrating specific-heat data, and indicate a significant change of behavior at ≈ 120 K (cf. Fig. 6 of Ref. 3); the two regimes can also be seen in resistivity data, where the changes are of opposite sign (cf. Fig. 5 of Ref. 6). Neu-

tron studies show that the initial reversion often involves the ordering of the polytype and $9R$ fractions between ≈ 90 and 120 K to produce the fcc phase, which then gradually reverts to bcc at temperatures up to 170 K, but leaving a highly strained sample.[12] These two regimes of structure correlate with the two regimes of reversion seen in Fig. 2, though further work is needed to show whether they are directly related.

In contrast with the data just discussed, the recent neutron-diffraction data,[13] and ultrasonic data,[17] (see also Ref. 18), on the *first* reversion curves of single crystals of lithium show little sign of the tail between ≈ 120 and 170 K. It is possible that absence of a tail indicates that reversion is there occurring in a single stage, without formation of the intermediate fcc phase, and in this connection very recent work on the effect of plastic strain on the transformation may be significant. Moderate deformation at 64 K (i.e., well below M_s) produced a strong (009)-$9R$ reflection, but apparently no other reflections from a well-defined $9R$ structure, only a very disordered polytype phase which began to revert *directly* to bcc at ≈ 100 K, without ever forming any fcc phase:[16] it is not clear how far the reversion region extends in this case, but it appears likely to be a single stage, at lower temperatures than when fcc is involved. In the present work, the shape of the reversion curves for the *higher* cycles was obtained less accurately, but all showed a marked reduction or even an absence of reversion above ≈ 130 K, which is consistent with a single, low-temperature reversion process, and perhaps the absence of the fcc phase.

The reversion curves without tails[13,17] are similar to those found for dilute LiMg alloys, where the resistivity shows large and symmetrical hysteresis loops.[6] For LiMg 0.21 at. % (where the transformation is ≈ 2 K higher than in pure lithium), the reversion runs from 95 to 125 K, with the 10–90% region occurring linearly between ≈ 100 and 110 K, with no tail; similar behavior is seen in the resistivity, and also in the specific heat of a 0.95 at. % alloy[4] ≈ 10 K higher. Single-crystal neutron diffraction on a much more concentrated alloy, LiMg 10 at. %, shows that here the low-temperature phase is $9R$ (with no appreciable polytype fraction), and that no fcc phase is formed during the reversion.[19] It appears that alloying has a simplifying effect on the transformation of lithium, possibly because it lifts the degeneracy in the free energies of the low-temperature phases, but probably also because it greatly affects its mechanical properties, even at low impurity levels. Dilute alloy studies could lead to a better understanding of the behavior of lithium but it already seems likely that the alloy data are simpler because the fcc phase plays no part. Whether the absence of the fcc phase is connected with the transformation strain field remains to be seen, but it is evident that there are large variations in the reversion curves for different samples of lithium, which remain to be elucidated.

(v) Ultrasonic measurements on lithium show large changes of sound velocity and attenuation as a result of the martensitic transformation. The changes seen in the single-crystal studies all show a rapid reversion between ≈ 90 and 110 K, with in some cases a small tail extending to ≈ 140 K, but then apparently rejoining *exactly* the curves on initial cooling.[17,18] For the velocity, this is not unexpected since the crystal has (usually) reverted to its initial structure and ori-
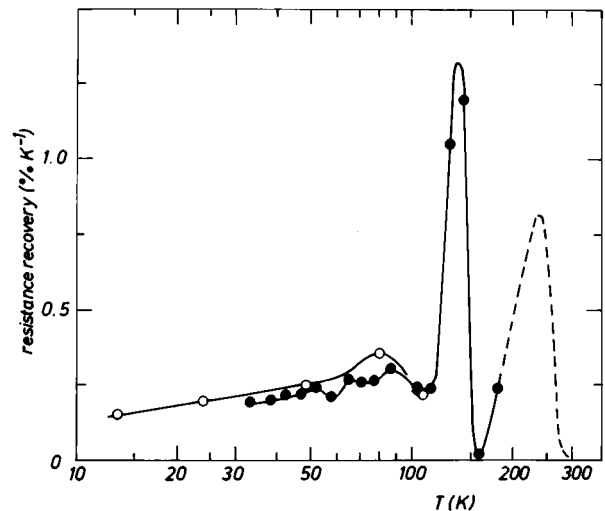

FIG. 3. The relative recovery of residual resistance for two samples of lithium extended by 5% at 4.2 K. The integrated area up to 110 K accounts for 20% recovery, while the large, sharp peak between 110 and 160 K accounts for a further 35%; the balance of 45%, which occurs below 300 K, was not measured in detail, and the dashed curve shows a conjectured form of this final, dislocation annealing peak.

entation, however, one would expect that the residual strain field (which often causes the crystal to break into a polycrystal at 250–300 K) should lead to increased attenuation. The earlier measurements on polycrystals, cf. Ref. 5, *did* show a much increased internal friction at the end of reversion (a 60% increase at ≈ 160 K; Verdini, private communication). Further information on the behavior of defects in lithium comes from the recovery of residual resistance after deformation at 4.2 K, shown in Fig. 3 (cf. Ref. 20). Below 110 K, there is only a featureless recovery; between 110 and 160 K, however, there is a prominent peak which corresponds to about 35% of the total resistance recovery. This peak has no counterpart in the recovery spectra of sodium or potassium, and is below the range where dislocations anneal, but it coincides exactly with the lithium reversion tail. The increase of residual resistance produced by deformation at 4.2 K is partly due to defect multiplication, but is also due to the increase of the electron-scattering rate as the low-temperature fraction is increased by cold work.[6] The converse processes during the recovery peak are probably due to the reduction of the electron-scattering rate as fcc reverts to bcc as a result of the thermodynamically driven reversion, but it must also include some reduction of defect density as in ordinary recovery. It is strange that this is not seen in the ultrasonic attenuation measurements.

The results of the present work can be summarized: (a) the magnetic susceptibility of lithium increases by *at least* 26% on forming the low-temperature phase; (b) the variation of the increase on initial cooling suggests that the different close-packed structures may have appreciably different values of susceptibility as a result of their different Fermi surfaces; (c) the transformation is almost completely suppressed by simple thermal cycling, in direct conflict with experiments on the magnetoresistance; (d) the reversion in pure

lithium (but not in LiMg alloys) occurs in two stages, with a sample-dependent change over at ≈ 120 K, which may be related to the reversion of the fcc phase; and (e) the reversion in pure lithium is associated with a prominent peak in its residual resistance recovery spectrum.

The discussion shows that there are many problems in the interpretation of the data on the bulk electronic properties of lithium, and although the improved knowledge of the struc-

tural behavior sheds some light on them, much more experimental work needs to be done, ideally by making both structural and electrical/magnetic measurements on the same sample. Magnetic susceptibility can play an important role in this program, since it can give a sensitive and continuous measure of the changes under different thermal histories, for different sample treatments, and for controlled impurity doping.

[1] C. S. Barrett and C. R. Trautz, Trans. AIME **175**, 579 (1948).

[2] C. S. Barrett, Acta Crystallogr. **9**, 671 (1956).

[3] D. L. Martin, Proc. R. Soc. London, Ser. A **254**, 444 (1960).

[4] D. L. Martin, Can. J. Phys. **38**, 25 (1960).

[5] L. Verdini, *Proceedings of the Third International Congress on Acoustics*, edited by L. Cremer (Elsevier, Amsterdam, 1959), p. 480.

[6] J. S. Dugdale and D. Gugan, Cryogenics **2**, 1 (1961).

[7] D. Gugan and B. K. Jones, Helv. Phys. Acta **36**, 7 (1963).

[8] D. Gugan, Can. J. Phys. **41**, 1381 (1963).

[9] F. T. Hedgcock, Phys. Rev. Lett. **5**, 420 (1960).

[10] H. Lueken, Z. Naturforsch. A **33a**, 740 (1978).

[11] A. W. Overhauser, Phys. Rev. Lett. **53**, 64 (1984).

[12] W. Schwartz and O. Blaschko, Phys. Rev. Lett. **65**, 3144 (1990).

[13] H. G. Smith, R. Berliner, and J. Trivisonno, Phys. Rev. B **49**, 8547 (1994).

[14] V. G. Vaks *et al.*, J. Phys.: Condens. Matter **1**, 5319 (1989).

[15] R. Berliner *et al.*, Phys. Rev. B **40**, 12 086 (1989).

[16] Ch. Maier, O. Blaschko, and W. Pichl, Phys. Rev. B **55**, 113 (1997).

[17] D. Kubinski and J. Trivisonno, Phys. Rev. B **47**, 1069 (1993).

[18] J. Trivisonno, A. R. Slotwinski, and M. P. Johnson, J. Phys. (Paris), Colloq. **42**, C5-983 (1981).

[19] Ch. Maier *et al.*, Phys. Rev. B **51**, 779 (1995).

[20] W. S. C. Gurney and D. Gugan, Philos. Mag. **24**, 857 (1971).