Pressure effects on the martensitic transformation in metallic lithium

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High-resolution neutron-diffraction experiments have been performed on polycrystalline lithium-7 metal over a temperature and pressure range of 45 to 300 K and 1 bar to 6.5 kbar. The partial transition from the bcc phase to the 9R(Sm type) phase occurred at approximately 90 K at 6.5 kbar, about 15 K higher than the similar transition at 1 bar. On warming at 6.5 kbar, the 9R phase transformed to the fcc phase over a narrow temperature range near 140 K. Above 175 K only the bcc phase was present. Single-crystal measurements confirm the 9R to fcc transition even at atmospheric pressure.

Recent neutron-scattering experiments on both polycrystalline[1] and single-crystal[2] samples revealed that the low-temperature (< 75 K) form of metallic lithium is a combination of bcc and 9R(Sm type) phases coexisting uniformly throughout the samples. The ideal 9R structure[3,4] is a close-packed lattice consisting of hcp and fcc types of sites. Although Barrett[5] had interpreted the low-temperature x-ray results in terms of an hcp lattice, he showed that Li cold-worked at low temperatures became fcc. Barrett suggested that the thermodynamically stable form is actually fcc with a transition temperature of about 110 K. X-ray diffraction studies at room temperature by Frolov and Rodionov[6] to a pressure of 10 000 kg/cm^2 reported a transition to the fcc phase at 3000 kg/cm^2 (2.94 kbar), whereas Olinger and Shaner[7] in their room-temperature x-ray studies, using a diamond anvil apparatus between 30 and 100 kbar, did not observe a phase transition until 70 kbar was reached (also fcc). Resistivity measurements as a function of temperature and pressure by Lin and Dunn[8] revealed an anomaly at 260 kbar and 7 K, which they interpreted as evidence of a phase transition, perhaps even a superconducting transition.

There have been several theoretical studies of the most stable structures of Li as a function of crystal volume, but with conflicting results.[9-15] Some predict the fcc structure as the most stable while others predict hcp as the most stable, although the energy differences are small. One study[14] calculated the 9R structure as the most stable, but at volumes even greater than that at room temperature; at much smaller volumes other close-packed structures were favored. It should be noted that the

theoretical studies are effectively for $T = 0$, since finite-temperature effects have not been taken into account, although in some cases zero-point motion and the bulk modulus have been considered.

This neutron-diffraction study investigated the effects of modest hydrostatic pressures on the bcc-9R transformation temperature in a polycrystalline sample of ^{7}Li and a subsequent 9R-fcc-bcc transition on warming. A brief study of the 9R-fcc-bcc transition in a single crystal of natural lithium was also made. The details are described below.

A polycrystalline ingot of 99.99% ^{7}Li was cut to 2 in. in length and etched down to 0.4 in. in diameter in methanol. It was encased in a vanadium sheath in a He atmosphere. The details of the pressure vessel and the He gas pressurizing apparatus have been previously described,[16] except in this case the pressure vessel was fabricated from 7075 aluminum. The vessel was then attached to the cold tip of a Displex closed-cycle refrigerator mounted on the Special Environment Powder Diffractometer (SEPD) at the Intense Pulsed Neutron Source (IPNS) at the Argonne National Laboratory. The time-of-flight diffraction data were collected at a fixed scattering angle of $2\theta = 90°$. Cadmium masks were used to remove diffraction lines due to the Al pressure vessel.

The initial powder-diffraction scans were made at room temperature at atmospheric pressure and at 2.9, 4.5, and 6.5 kbar under hydrostatic conditions. There was no evidence of any transformation even though the volume change at 6.5 kbar was twice as large as the volume change from room temperature to 75 K at atmospheric pressure, at variance with the x-ray results of Ref. 6. The
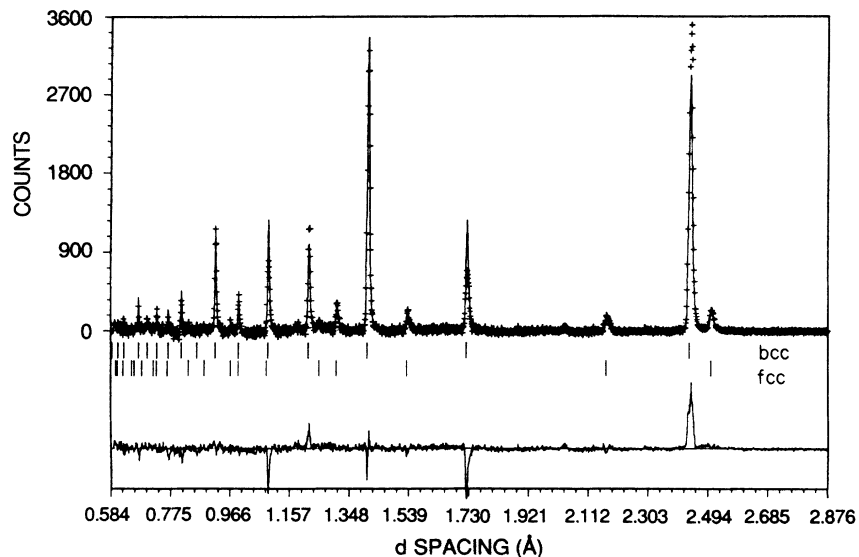
FIG. 1. Diffraction pattern at $T = 140$ K, $P = 6.5$ kbar (after cooling to 70 K); about 20% of the fcc phase coexists with the bcc phase.

fact that the bcc structure did not transform by volume changes alone suggests that theoretical total-energy calculations should include the effects of vibrational entropy in the search for the most stable structure, even at low temperatures. The sample was then cooled in stages down to 109 K, keeping the pressure as nearly constant as possible at 6.5 kbar. Upon further cooling to 90 K, a partial transformation to the 9R structure had taken place. This indicates T_c increased about 15 or 20 K above the atmospheric pressure T_c, or roughly 3 K/kbar of applied pressure. This ratio is similar to that obtained by Olinger and Shaner[7] in their room-temperature x-ray diffraction studies of Li in a diamond anvil apparatus at a pressure of 70 kbar, in which they reported a change to the fcc structure in their experiments.

Upon warming in stages from 70 to 140 K at maximum pressure, the 9R structure disappeared. A small amount (approximately 20%) of the fcc phase appeared (Fig. 1), and then disappeared on further warming to 175 K, leaving only the bcc phase. The pressure was reduced to about 300 bars and the sample cooled to about 45 K, where again about 50% of the bcc phase transformed to the 9R structure. A brief search was made on warming for the appearance of the fcc phase and none was observed. Perhaps the changes in temperature were too coarse. It should be mentioned that there have been very weak peaks observed in the earlier single-crystal data[2] that could be attributed to a very small amount of fcc phase. Even in the polycrystalline data[1] there is a slight indication of a (200) fcc peak. Alternatively, these weak peaks could be evidence for a more complex unit cell than the 9R rhombohedral structure.

The possible existence of the fcc phase was investigated further with a single crystal at atmospheric pressure on a triple axis spectrometer at Riso National Laboratory. This was accomplished by monitoring the intensity at the positions of the (104) and (103) 9R reflections while slow-

ly warming the sample after the 9R transformation. The intensity of the (103) reflection is zero for the 9R structure, but not for the fcc structure indexed on the 9R lattice [with proper fcc index of (111)]. Figure 2 shows the decrease in intensity of the strong (104) 9R reflection (which began at about 90 K), while the (103) 9R reflection increases, clearly indicating the growth of the fcc phase at the expense of the 9R phase, but not necessarily on a volume-for-volume basis.
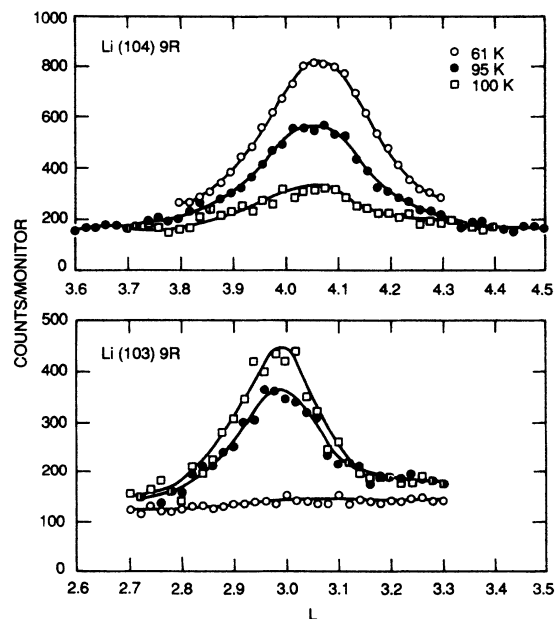

FIG. 2. Intensities of the (104) 9R and (103) 9R [(111) fcc] reflections at 61, 95, and 100 K. The scans are along the 10L line in reciprocal space.

TABLE I. Lattice constant of bcc ^{7}Li vs temperature and pressure.

T (K)	P (kbar)	a_0 (Å)	Run No.
300	10^{-3}	3.5130(1)	2410
300	2.9	3.4848(2)	2411
300	4.5	3.4727(1)	2412
300	6.5	3.4562(1)	2413
150	6.5	3.4379(1)	2414
109	6.5	3.4340(1)	2416
140[a]	6.5	3.4363(1)	2422
90	2.7	3.4627(1)	2425
90	5.1	3.4439(1)	2426

[a]After cooling through the 9R transformation to 70 K.

If the 9R phase was metastable with respect to the fcc phase, it is possible that the amount of the fcc phase could be increased relative to the 9R phase by repeated cycling through T_c, somewhat analogous to a strain-anneal crystal-growth process. A series of annealing cycles at atmospheric pressure were subsequently performed on a polycrystalline sample at IPNS. The results were not conclusive that the fcc phase appeared at all on warming, and certainly did not grow upon repeated cycling through T_c.

The initial scan at $P = 1$ bar and $T = 300$ K showed a small amount of preferred orientation in the bcc phase, but this increased somewhat with increasing pressure and decreasing temperature and was largest after the 9R to fcc transformation took place, as shown in Fig. 1 by the difference pattern. A Rietveld refinement of these data at $P = 6.5$ kbar and $T = 140$ K indicated about 20% of the sample was fcc and the remainder bcc. The lattice constants were determined to be a(bcc) $= 3.4361(1)$ Å and a(fcc) $= 4.3271(5)$ Å with nearly identical atomic volumes, V(bcc) $= 20.285$ Å^3 and V(fcc) $= 20.255$ Å^3. The lattice constants are listed in Table I for several temperatures and pressures. The results are in reasonable agreement with the compressibility studies of Anderson and Swenson,[17] and Vaidya, Getting, and Kennedy.[18]

The data at $T = 70$ K and $P = 6.5$ kbar are shown in Fig. 3. About 50% of the bcc phase has transformed to the 9R phase. Because some of the 9R peaks are broadened and shifted from their ideal positions, indicative of severe stacking fault behavior, it was not possible to do a Rietveld least-squares refinement on this phase.

The results of these experiments are at variance with the x-ray studies of Frolov and Rodionov[6] in which a bcc to fcc transition occurred at 2.94 kbar at room temperature. Their data were obtained by photographic methods, but the pressure techniques used are uncertain; however, it is likely that nonhydrostatic methods were used, in contrast to the hydrostatic conditions in the He gas pressure
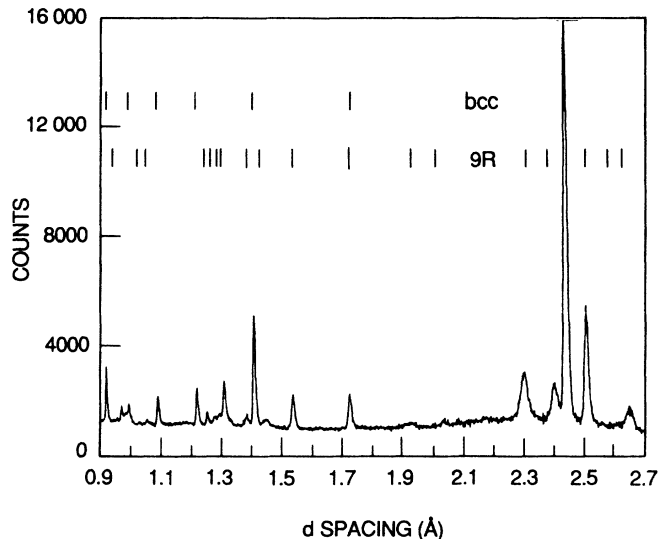

FIG. 3. Diffraction pattern at $T = 70$ K, $P = 6.5$ kbar (bcc and 9R phases coexist in approximately equal amounts).

system used in the neutron studies. The large discrepancy in transformation pressure between the two x-ray studies in which Olinger and Shaner[7] reported an fcc transition at 70 kbar at room temperature and the low-pressure experiments[6] is not resolved, but may be due to the methods of applying pressure. Clearly much work needs to be done to fill in the gap between the low- and high-pressure regions.

In summary, the application of hydrostatic pressure of 6.5 kbar to a polycrystalline sample increased the transformation temperature of the bcc to 9R structure from about 75 to 90 K. On warming, at this pressure, the 9R structure transformed to the fcc structure between 110 and 140 K, which then transformed back to the bcc structure on further warming. Measurements on a single crystal at atmospheric pressure revealed the presence of the 9R to fcc transition in the temperature range of 90–100 K, which then, on warming, slowly transformed back to the bcc phase.

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