

Crystal Structure of Lithium at 4.2 K

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The (heretofore unknown) crystal structure of lithium at low temperature is identified to be close-packed rhombohedral $9R$. The stacking order of the hexagonal layers is $ABCBCA-CAB$, a nine-layer repeat sequence. There are three atoms per primitive rhombohedral cell, and nine in the (nonprimitive) hexagonal cell. The only other element with this structure is samarium.

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It seems surprising that the ground-state crystal structure of metallic lithium has remained unknown. In common with the other alkali metals it is body-centered-cubic (bcc) at room temperature. In 1948 Barrett and Trautz¹ discovered that Li undergoes a structural phase transformation on cooling below 70 K. They suggested that the new phase was hexagonal-close-packed (hcp). However, a recent study² has shown that the structure is neither hcp nor face-centered-cubic (fcc).

Determination of the atomic arrangement is difficult in this case because single crystals of the low-temperature phase are not available. Only polycrystalline diffraction patterns have been obtained. The best work² employed 1.06-Å neutrons. The 4.2-K data of this study show no trace of an hcp (012) reflection; the hcp (011) line is also missing. Neither is there an fcc (200) reflection. So the most common close-packed structures have been eliminated as possibilities.² The hexagonal-layer stacking sequences of the hcp and fcc lattices are $ABAB$, . . . , and $ABCABC$, They can be denoted $2H$ and $3R$.

During the following discussion the reader should refer to Figs. 1 and 2 of Ref. 2, which are "powder" patterns for $\lambda = 1.06$ Å. Perhaps the next stacking sequence to try is the "double hcp" (or $4H$) structure $ABACABAC$, . . . , with a repeat distance of four. Several elements have this structure, e.g., La, Ce, Pr, Nd, and Am. Such a crystal must have an (014) reflection, at 33.3° , which is equivalent to the (012) line of the hcp lattice. As mentioned above, this line is not present. The stacking sequence $ABCACB$, which might be called "triple hcp" (or $6H$), does not have a reflection at 33.3° ; but its (014) reflection, at 27.9° , coincides with the (200) fcc line, which is also missing.

A somewhat more complex arrangement of hexagonal layers is the $9R$ sequence of samarium: $ABCBCACAB$. The primitive rhombohedral cell has three atoms, but the hexagonal cell has nine.

The scattering angles and structure factors $|F|^2$ for the first 26 diffraction lines are given in Table I. The lattice parameter $a = 3.111$ Å, in the hexagonal plane, has been taken from Barrett³ since the Bragg angle θ_B of the dominant new line, (110), of the low-temperature Li phase does not depend on the stacking sequence along the c axis. Other θ_B are based on the assumption that ideal close packing obtains, i.e., $c = 9(\frac{2}{3})^{1/2}a = 22.86$ Å.

The calculated diffraction pattern of the $9R$ structure appears to agree well with the observed spectrum.² Before a discussion of details one should note that approximately 75% of the sample transforms from bcc to the new phase on cooling to 4.2 K. The diffraction pattern continues to change (at 4.2 K) during the first 24 h.² The peak heights

TABLE I. Diffraction lines of the $9R$ structure with $a = 3.111$ Å and $c = 9(\frac{2}{3})^{1/2}a$, appropriate to Li at 4.2 K. The structure factors $|F|^2$ for (009) and (0018) have been divided by three to account for the reduced multiplicity (2 compared to 6) relative to all others. A neutron wavelength $\lambda = 1.06$ Å has been assumed in calculating the scattering angles $2\theta_B$.

(hkl)	$2\theta_B$	$ F ^2$	(hkl)	$2\theta_B$	$ F ^2$
101	22.85	1.8	202	46.68	0.8
012	23.32	0.8	119	47.10	9
009	24.09	"3"	024	47.68	6.4
104	25.12	6.4	205	48.43	6.4
015	26.40	6.4	0018	49.33	"3"
107	29.55	0.8	1016	49.65	0.8
018	31.37	1.8	027	50.38	0.8
1010	35.40	1.8	208	51.57	1.8
0111	37.58	0.8	0117	52.27	1.8
110	39.84	9	0210	54.34	1.8
1013	42.19	6.4	2011	55.92	0.8
0114	44.61	6.4	1019	57.69	1.8
021	46.42	1.8	0213	59.42	6.4

near 23° and 26.5° almost double. This behavior cannot be attributed to further conversion from the bcc phase, since full conversion would lead to only a 33% increase. (Indeed, significant intensity remains in the bcc reflections after 24 h.) Instead, the changes occurring at 4.2 K must be caused (primarily) by annealing of stacking faults in the new phase. Such behavior is expected in any long-period structure.

McCarthy, Thompson, and Werner² noted that the first reflection near 23° was too small by a factor of about 8 for an hcp reflection. The first two lines (near 23°) of the 9R phase have combined intensity, $|F_1|^2 + |F_2|^2$, of 2.6. A full-strength hcp line on this scale would have an intensity of 18, twice the maximum number in Table I (on account of the extra multiplicity, 12 instead of 6, for hexagonal powder patterns compared to rhombohedral). Thus the unresolved pair at 23° should be 7 times weaker than a full-strength hcp line. In Fig. 2 of Ref. 2 the shoulder *A* at 24° and the peak at 26.5° correspond to the (009) and (015) reflections of 9R. The (104) cannot be separated from the (residual) bcc (110). The two shoulders labeled *B* in Fig. 1 of Ref. 2 are the 9R (1013) and (0114). A high-resolution study in this region would allow an accurate determination of the lattice parameter *c*. The reflections in Table I between 29° and 38° are either too small to identify or are masked by the Al (200), from the sample holder, or by the Li bcc (200). The large asymmetric structure (in Fig. 1 of Ref. 2) between 47° and 50° is explained very well by the four 9R reflections in this region. Here, also a high-resolution study will provide a rigorous test of the proposed 9R phase, provided stacking faults are eliminated by annealing.

The low-temperature phase of Li is of particular interest because Li is not superconducting, at least not above 6 mK. Calculations of the electron-phonon interaction parameter⁴ show that $\lambda \approx 0.4$, which would imply a superconducting transition temperature $T_c \sim 1$ K. (The calculations apply, of course, to the bcc phase.) One expects that, among all metals, prediction of T_c should be most reliable in one so simple. Therefore failure by a factor of at least 100 is quite disturbing.

A comparison of the theoretical values of λ in the bcc and 9R structures becomes a fascinating question. Possibly the "loss" of the slow shear modes (of the bcc structure) can lead to a significant reduction in λ for the 9R. On the other hand, the Fermi surface in the 9R phase is near 38 energy-gap planes, compared to 12 for the bcc (and 14 for an fcc). This could lead to enhanced electron-phonon umklapp coupling associated with low-frequency phonons, and to a larger λ .

One may anticipate that the interband optical absorption spectrum of the 9R phase will differ substantially from that⁵ of the bcc on account of the drastic alteration in energy-gap configuration. Prediction of this is a real challenge since an experimental check is relatively easy.

¹C. S. Barrett and O. R. Trautz, *Trans. Am. Inst. Min. Metall. Pet. Eng.* **175**, 579 (1948).

²C. M. McCarthy, C. W. Thompson, and S. A. Werner, *Phys. Rev. B* **22**, 574 (1980).

³C. S. Barrett, *Acta Crystallogr.* **9**, 671 (1956).

⁴G. Grimvall, *Phys. Scr.* **12**, 337 (1975).

⁵T. Inagaki, L. C. Emerson, E. T. Arakawa, and M. W. Williams, *Phys. Rev. B* **13**, 2305 (1976).