Martensitic Phase Transformation of Single-Crystal Lithium from bcc to a 9*R*-Related Structure

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A neutron elastic- and inelastic-scattering study of single-crystal bcc lithium was performed above and below the martensitic phase transformation in the vicinity of 75 K. The transformation is abrupt and the bcc lattice partially transforms to a 9*R*-related (Sm-type) structure. The 9*R* c^* and a^* axes of this variant are nearly along the [110] and [1$\bar{1}$0] bcc directions, respectively. The (10*L*) and (20*L*) 9*R* reflections were broadened and shifted from their ideal positions compared to the (00*L*) 9*R* reflections, indicative of numerous stacking faults. On warming, the sample reverts back to a single crystal with the same bcc orientation.

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Lithium, in spite of its being the lightest metal and also having the smallest number of electrons, exhibits rather complex behavior in some of its physical properties. Barrett and Trautz[1] observed a partial structure change by x-ray diffraction in the vicinity of 75 K. It appeared to be a mixture of untransformed bcc lithium plus an hcp phase. An fcc phase could be obtained by cold working at low temperatures.[2] Specific-heat measurements by Martin[3] revealed a long hysteresis on warming from below the phase transition. Inelastic-neutron-scattering studies of the lattice dynamics of Li[4,5] at 98 K showed an unusual crossing over of the LA[100] branch below the TA[100] branch.

The present study of single-crystal lithium was undertaken for several reasons: (1) the discovery[6-8] of the 9*R* structure coexisting with the bcc lattice by a neutron-scattering study of polycrystalline lithium at low temperatures; (2) the discovery of charge-density waves in potassium[9]; and (3) the desire to extend the previous phonon measurements below the phase transition. In the meantime, a paper by Ernst *et al.*,[10] appeared describing a neutron-scattering study of single-crystal ^{7}Li above and below the phase transition. At 74 K they observed an extra reflection near the (110) bcc lattice point, which they indexed as (002) hcp, but they conceded that it could be the (009) 9*R* or some other close-packed hexagonal lattice reflection. They also observed a softening of the entire Σ_4 branch with a slight dip occurring at a $\mathbf{q}$ of $(0.4,0.4,0)2\pi/a$. The previous inelastic neutron-scattering studies did not show softening of the entire branch nor the dip at $(0.4,0.4,0)2\pi/a$; indeed, a slight hardening of this branch at low q values had actually been observed.

This study, using single crystals of natural lithium, confirms the growth and orientation of a 9*R*-related (Sm-type) structure in the bcc lattice, and photographs of the Bragg reflections show that both types of reflections are coming from the entire crystal. The sample reverts to a single crystal of bcc Li on warming. These experiments and others are described below.

Three single crystals of natural lithium of excellent quality (FWHM = 0.2°, instrumental resolution plus mosaic width) were used. Crystal B (5 cm long by 1 cm diameter), obtained commercially, was the same one used in the lattice-dynamics study[4] nearly twenty years ago. The other crystals, A and C (3 cm long by 1 cm diameter), were kindly furnished by J. Trivisonno. The elastic- and inelastic-neutron-scattering measurements were made on the HB-3 and HB-1A triple-axis spectrometers at the High Flux Isotope Reactor employing both Be and pyrolytic graphite monochromators and analyzers and a pyrolytic graphite filter, with neutron energies of 3.6, 5, and 8.5 THz.

Careful searches were made for possible satellite peaks in crystal A near the (110) bcc reflection just above the transformation temperature (thought to be around 75 K), as had been observed in potassium. The results were negative, but, because of the large background (described below), it is estimated that the smallest observable satellite would be of the order of 10^{-4} of the (110) bcc reflection, about 100 times less sensitive than that observed in the experiment on potassium. Also, only a small region of reciprocal space was explored, and so it is conceivable that charge-density wave reflections could exist elsewhere in the Brillouin zone or within Δq of <0.03 of the (110) bcc reflection along the [110] direction. A structureless temperature-dependent background was observed as had been reported by McCarthy, Tompson, and Werner[6] and by Ernst *et al.*[10] The former group interpreted this scattering as spin incoherent scattering from the ^{7}Li nucleus, whereas the latter group suggested that it was due to defects in the bcc lattice. The nonnegligible spin incoherent scattering will increase in intensity with decreasing temperature just as the intensities of the Bragg reflections do. This scattering must be subtracted from the total scattering in order to determine the amount of defect scattering.

As the temperature was lowered an abrupt decrease in peak intensity of the (110) bcc reflection was observed at about 74 K and a series of scans were made in the vicinity of this reflection. A pronounced peak was observed at the reciprocal-lattice position (0.920,1.018,0) when the bcc crystal axis was tipped about 2.5° out of the scattering plane. The FWHM of this reflection [indexed as (009) 9*R*, as suggested by the low-temperature polycrystalline studies] and the (110) bcc reflection had increased to about 1°. The second order of this reflection at (1.850,2.036,0) was also observed, as well as a similar first-order peak near the $(1\bar{1}0)$ bcc reflection. The sample was further cooled to 60 K and the integrated intensity increased while that of the (110) bcc decreased. The FWHM increased to 1.6°. Neutron-diffraction photographs of the (110) bcc and (009) 9*R* reflections were identical except for overall intensity indicating that the new structure is uniformly embedded in the bcc lattice. Because of secondary extinction and its dependence on mosaic spread, it is difficult to determine precisely how much of the crystal transformed, but it is estimated to be of the order of 50%. The crystal was then slowly heated to 200 K while we observed this new reflection. There was little change in intensity until about 110 K when the peak intensity started decreasing more rapidly; however, there was still an easily measurable remnant at 160 K, which disappeared entirely by 200 K. The crystal had reverted back to a completely bcc single crystal. The FWHM had decreased to about 1.3° indicating that some annealing of the strains had taken place.

On the next cooling cycle the transformation appeared to occur at a lower temperature (68.4 K on the sensor), but it is possible that the sample temperature had not yet stabilized. On lowering of the sample temperature to 59 K the FWHM increased to about 2°. The sample was then warmed up to room temperature with the hope of annealing the strains, but instead, it broke up into several grains. One grain (about $\frac{1}{4}$ of the sample) was reoriented as before; its FWHM had decreased to 0.5°, indicating a relief of the strains in the individual crystals. On cooling, this grain transformed abruptly at 72.5 K over a time interval of 6 sec, as shown in Fig. 1. On the next cycle the sample was virtually destroyed.

Later, crystal B was slowly lowered through the phase transition, which occurred in this case at 78 K, perhaps an hour or more after reaching this temperature. A reflection was again observed at (0.920,1.018,0), but a much stronger variant was observed at (1.019,0.924,0), again about 2.5° out of the $(hk0)$ bcc scattering plane. It was indexed as (009) 9*R* and a search was made for other 9*R* reflections. By tilting of the $[1\bar{1}0]$ axis approximately 5° out of the scattering plane, the $(H0L)$ and $(H0\bar{L})$ reflections of the Sm-type structure were observed. The relation of this variant to the bcc reciprocal lattice is shown in Fig. 2. The 9*R* c^* and a^* axes are nearly along the [110] and $[1\bar{1}0]$ bcc directions, respectively. The $[1\bar{2}0]$ 9*R* direction is nearly parallel to the [001] bcc direction. Many other variants of different orientations are expected to exist and could confuse a search for other reflections such as charge-density-wave satellites. The aluminum sample container with its powder lines and texture spots also contribute extra

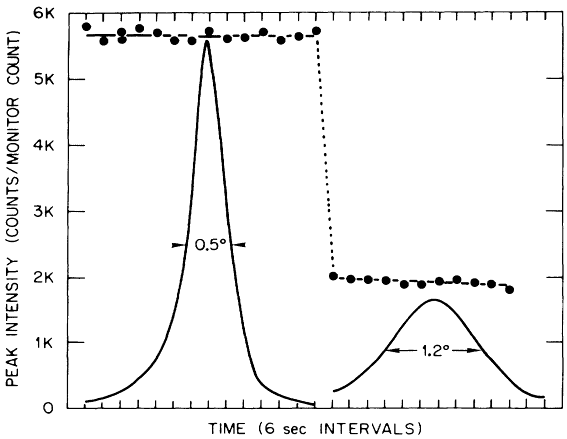

FIG. 1. Intensity of the (110) bcc reflection vs time (6-sec intervals) at $T=72.3$ K. The change in peak shape slightly above and below the transition is also shown.

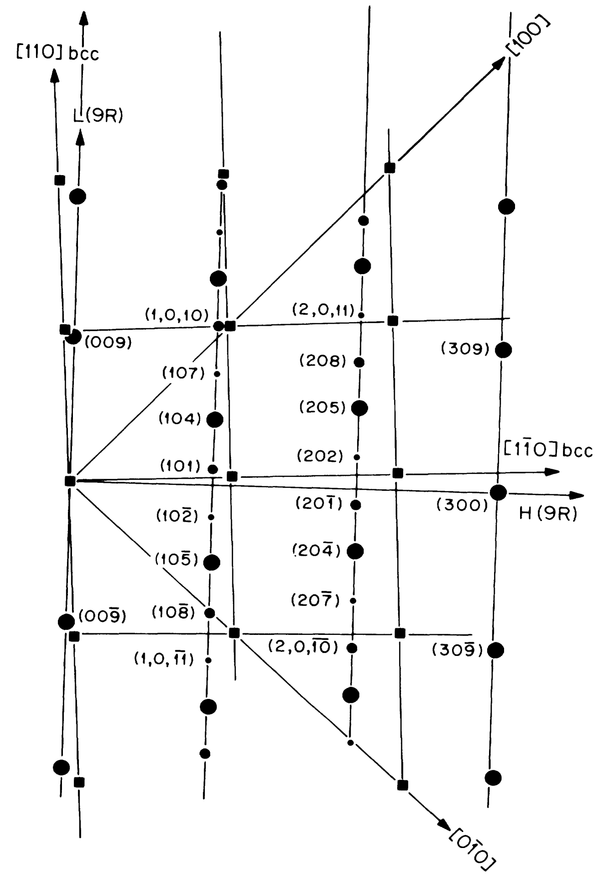

FIG. 2. Relation of one variant of the 9*R* structure to the bcc reciprocal lattice.

peaks; however, these peaks were eliminated when the third crystal, C, was mounted in a vanadium container which produces no powder lines.

It was readily apparent that the effects due to stacking faults as evidenced in the polycrystalline studies were even more pronounced in the single-crystal studies. For example, the (101) 9*R* reflection, which essentially showed no shift or width in the earlier polycrystalline studies, was quite broad and shifted to (1,0,0.89) 9*R* in this experiment. This is because the transverse displacement cannot be readily observed in the polycrystalline sample at this low *L* value. The outward shifts of the (1 0 4) and (1 0 13) reflections and the inward shifts of the (1 0 $\bar{5}$) and (1 0 $\overline{14}$) reflections are in qualitative agreement with the experimental and theoretical results of the polycrystalline studies,[6] but the shift of the (101) 9*R* and ($\bar{1}$02) 9*R* reflections mentioned above are opposite to those calculated. The peak shifts and widths along with the diffuse streaking between reflections indicate a high degree of faulting, but weak extra peaks are observed which suggest a deviation from true rhombohedral symmetry. Further detailed studies will be necessary to clarify this situation.

Phonon dispersion studies of the Σ_4 branch, [110] propagation with [1$\bar{1}$0] polarization, as a function of temperature confirmed the earlier published and unpublished results[4] that there is no pronounced soft mode along this branch. At low q, <0.25, the phonon frequencies are slightly higher than at room temperature, in agreement with the elastic-constant results.[11] There is a small decrease in frequencies out to the zone boundary reaching a change of about 8% at $q = 0.5$, but no dip was seen at $q = 0.4$ (see Fig. 3), contrary to that reported by Ernst *et al.*[10] The phonon positions were well determined to about (1–2)%. It was concluded that attempts to measure the phonon dispersion curves of bcc Li with up to 24 variants of the 9*R* structure would be unproductive.

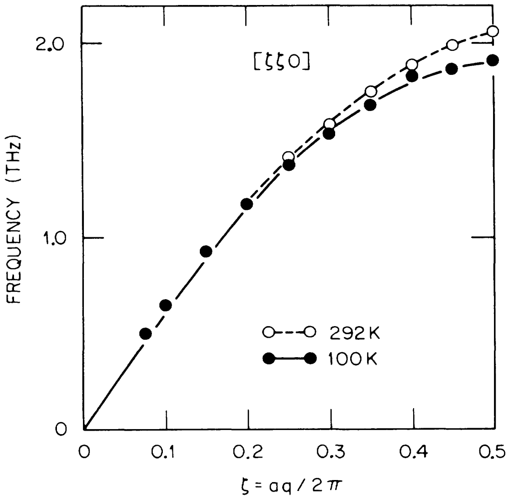

FIG. 3. Dispersion curve of the Σ_4 branch of bcc Li at 100 K. The dotted line represents the data obtained at 292 K.

It is generally accepted that the transition from bcc to hcp or fcc, which is so common in many metal systems, involves a distortion in the (110) planes and a shearing or "shuffling" motion parallel to these planes. In the former, motion of the tetrahedral angle of 109°26′ to exactly 120° is required and the nearest-neighbor distance is essentially preserved. The latter shearing motion produces the *ABAB*... or *ABCA*... stacking sequences in the *c* direction of the hexagonal or trigonal lattice with displacements of the order of $\frac{1}{3}$ the nearest-neighbor distance.

The crystal structure of the samarium lattice along with its inherent disorder has been fully described previously.[12] The differences between Sm and the 9*R* lithium lattice embedded in the bcc lattice will be briefly discussed below; a more complete discussion will follow in a full publication after a more extensive analysis of the stacking faults. The lattice constants observed at 78 K of the coexisting Li structures are the following: $a(\mathrm{bcc}) = 3.483(2)$ Å, volume/atom $= 21.12$ Å^3, and $a(9R) = 3.103(2)$ Å, $c(9R) = 22.795$ Å, $\gamma = 120°$, $c/a = 1.6325$, $v/a = 21.12$ Å^3. The space group of the 9*R* structure is actually $R\bar{3}m$, $a(R) = 7.807$ Å, $\alpha = 22.93°$ with atoms at (000) and $\pm(xxx)$ where $x \cong \frac{2}{9}$. With hexagonal indexing the atoms are at (000), $\pm(00z)$; $+\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ and $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$ with $z \cong \frac{2}{9}$. Only those reflections that satisfy the condition $-H+K+L=3n$ are allowed. If $z \equiv \frac{2}{9}$ one has true close-packing with the sequence ...*C*/*ABABCBCAC*/*A*..., which is sometimes written as *h*/*chhchhchh*/*c*, illustrating the type of close packing about a given atom. Note that *z* does not have to be exactly $\frac{2}{9}$ and, therefore, all layers do not have to be equally spaced. There is some evidence that this may be the case in lithium, which will be investigated in the fuller publication. An alternative description can be *ABC*/*A′B′C′*/*A″B″C″* where each 3-layer sequence is arranged in a cubic-close-packed arrangement. This description may be of some significance in discussion of the nature of the stacking faults, which may be highly correlated. A projection of the 9*R* structure is shown in Fig. 4. A possible orientation of the bcc lattice as suggested by the experimental data is indicated on the right. The description of the martensitic transformation in the β-phase alloy Ag-Cd in terms of 9*R* and 18*R* structures[13] does not seem to be appropriate to Li; however, the recent description by Wilson and de Podestal[14] of the possible 9*R* formation in bcc K is not too different from that described in this paper [although their explanation of the charge-density-wave satellites in terms of embryonic martensites of the 9*R* structure is inadequate to explain the *four* satellites about the (110) bcc reflection].

The diffraction pattern of Li is somewhat different

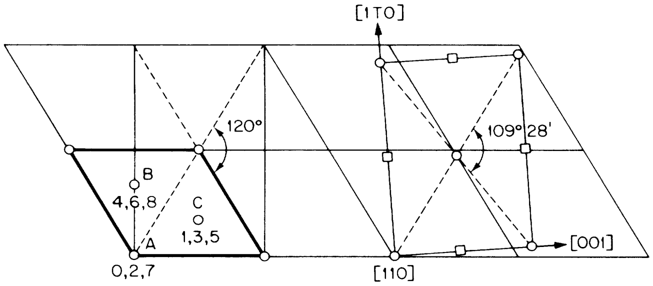

FIG. 4. Projection of the $9R$ structure onto the (001) plane. The numbers at the atomic positions indicate the height above the $z=0$ plane in units of $c/9$. The ortho-hexagonal lattice is also outlined. A possible orientation of the bcc structure as suggested by the experimental data is indicated on the right. The [110] direction is tilted about 5° from the normal to the plane of the paper.

from that of Sm. In the latter, the $(H0L)$ reflections were identical to the $(H0\bar{L})$ reflections, contrary to a rhombohedral lattice; but this was explained in terms of a twinning-fault disorder, which does not shift the reflections from their ideal positions, as observed so strongly in Li. The observed shifts in Li have been interpreted[8] in terms of deformation faults rather than twinning faults; however, powder-diffraction data alone cannot rule out the existence of twin faults. The absence of any peaks at the (014) $9R$ or $(\bar{1}05)$ $9R$ positions in the single-crystal studies is strong evidence that twin faults are minimal.

These preliminary results described above show that the martensitic transformation in lithium metal in the vicinity of 75 K is a first-order partial transformation from the bcc structure to a $9R$-related structure with numerous stacking faults. The two lattices coexist throughout the sample and revert back to a single crystal of bcc lithium at about 170 K. It is hoped that these experimental results will stimulate theoretical studies of the phase transition in Li. An electron microscopy examination above and below this transformation should be very illuminating.

If additional single-crystal samples of good quality can be obtained, particularly one grown with the nonabsorbing ^{7}Li isotope, much more detailed investigations at lower temperatures will be undertaken.

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