Polytype Structures of Lithium at Low Temperatures

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After cooling below 80 K a considerable amount of diffuse scattering is observed in Li, in addition to 9*R* and fcc Bragg reflections. The diffuse scattering localized on the [101] line of the 9*R* reciprocal lattice is modulated along this line, indicating a short-range order in the stacking sequence of the close-packed planes. The results show that, in addition to the long-range ordered fcc and 9*R* structures, Li forms at low temperatures a disordered polytype where short-range ordering tendencies of the hcp, fcc, and 9*R* types are simultaneously present. These observations may be explained in terms of competing cubic and hexagonal ordering tendencies in the stacking sequence of close-packed planes.

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The structure of lithium metal below the martensitic phase transition near 70 K was the subject of a series of recent investigations. Interpreting powder-diffraction data of McCarthy, Tompson, and Werner.[1] Overhauser[2] proposed for the low-temperature phase of lithium the 9*R* structure characterized by a nine-layer sequence of close-packed planes (*ABCBCACAB*). Subsequent neutron-diffraction experiments[3–7] found indeed a faulted 9*R* structure in lithium below 70 K. These observations are at variance with the early structure determination by Barrett[4] who proposed a faulted hcp lattice. Recently, Smith *et al.*[5] observed during the back transformation that the 9*R* volume fraction first became partially fcc before reverting to the high-temperature bcc phase.

In the present Letter we report results of an experiment on the low-temperature phase of lithium by diffuse-neutron-scattering techniques. The experiment shows that some amount of fcc is always present concomittantly with the 9*R* structure in its whole range of stability. In addition to sharp 9*R* reflections, a considerable amount of diffuse scattering is observed. This diffuse scattering is localized in the [101] direction. This observation gives evidence for the presence of a disordered polytype structure where the stacking sequence of close-packed planes shows no long-range correlations.

At temperatures above 80 K the disordered polytype and the 9*R* structure transform to a perfect fcc lattice. In view of these observations arguments are put forward that the 9*R* structure is formed from fcc-type nuclei in order to reduce the coherency stresses with the bcc matrix.

The experiment was done on the triple-axis spectrometer VALSE located at a cold-neutron guide position of the Orphée reactor in Saclay. In order to eliminate higher-order contaminations a pyrolitic graphite filter was put into the incident beam. Three single crystals each of about 2 cm^3, grown from the same ^7Li material, with an initial mosaic spread of about 30 min were investigated. The samples were mounted in a closed-cycle cryostat. All crystals were cylindrical with a diameter of 10 mm. They were packed under argon atmosphere in an aluminum container with a diameter slightly larger than the crystals. A small spring applying a pressure of about 10 N/m^2 was enclosed between the top of the cylinder and the container in order to prevent an accidental rotation. As the thermal expansion of lithium is larger than that of aluminum, no additional stresses should be induced during the cooling procedure. The differences in the observed transformation behavior between the three crystals should therefore be due to differences in the initial defect structure and in the applied cooling procedures. Although the relative amount of the different polytype structures varied from sample to sample, the experiment shows that the essential characteristics of the scattering pattern, i.e., the presence of disordered and short-range-ordered polytype intensities, were similar for all three samples investigated.

The first crystal was cooled down to 72 K, where the presence of four peaks in the vicinity of the (110) bcc fundamental reflection indicated that the bcc lattice had partially transformed to different variants of the low-temperature phase in accordance with the orientation relations known from previous experiments.[3,6] At 72 K the intensity of the (110) bcc reflection has decreased by about 25%. As extinction effects may be important, this Bragg intensity decrease gives only a lower limit for the amount of transformed material. An investigation of small-q phonons of the transverse acoustic $TA_1[110][1\bar{1}0]$ branch showed indeed between 80 and 72 K an intensity reduction of 35%, which indicates a somewhat higher volume fraction for the transformed bcc material. Elastic scans along the [101] direction of the strongest variant revealed in addition to sharper 9*R* reflections the following diffuse features (Fig. 1). An intensity ridge extends over a wide region of the [101] direction; i.e., the dash-dotted line in Fig. 1 shows the background level determined from outside but adjacent regions of the [101] line. The intensity ridge extends out to (1,0,10) and $(1,0,\bar{10})$ positions, respectively, and within the resolution is well localized on the [101] line as

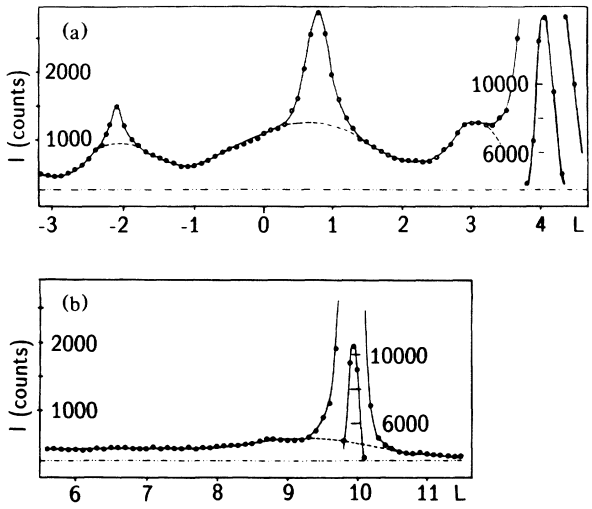

FIG. 1. (a) Diffuse intensity distribution along a segment of the [101] $9R$ line observed in the first Li crystal at 72 K. The dash-dotted line indicates the background level determined from adjacent regions of the [101] direction. The dashed line shows the modulation of the diffuse intensities, especially a maximum near (103) corresponding to a (111) fcc position. The sharper peaks are $9R$ reflections. (b) Diffuse intensity distribution along another segment of the [101] $9R$ line. The symbols are the same as in (a). The figure shows the extension of the intensity ridge on [101] and a broad distribution near (109) corresponding to the (102) hcp position. In the figure the (1,0,10)-$9R$ peak intensity is contaminated by the (200) bcc matrix reflection. The two reflections cannot be resolved by their nearly identical lattice spacing. Moreover, from the orientation relations observed the two reflections are also nearby in reciprocal space. A resolution calculation shows that about 50% of the measured intensity at the (1,0,10)-$9R$ point comes from the strong (200) bcc reflection.

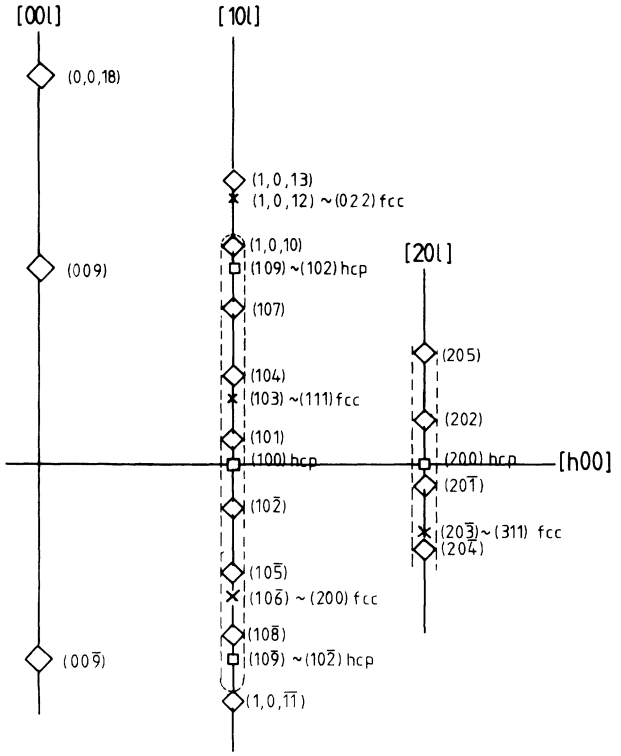

FIG. 2. Schematic representation within the $9R$ reciprocal lattice of the diffuse intensities found in Li below 80 K. ◇, $9R$ positions; ×, fcc position; □, hcp positions. The dashed line indicates the intensity ridge.

confirmed by scans perpendicular to [101]. The diffuse intensity shows some modulation along [101] with broad maxima near the (101) and (10$\bar{2}$) $9R$ positions. In addition, diffuse maxima are observed near (103), (10$\bar{6}$), and (1,0,12) points corresponding to the positions of (111), (200), and (022) fcc reflections, respectively (Fig. 2). Moreover, near (109) and (10$\bar{9}$) $9R$ positions corresponding to (102) and (10$\bar{2}$) hcp reciprocal-lattice points diffuse intensities were found [Fig. 1(b)].

Near $l=3n+1$ sharp $9R$ reflections are observed. They are shifted somewhat from their ideal positions in qualitative agreement with previous works.[7] From the width of the $9R$ reflections varying between 0.15 and 0.30 in units of l it can be estimated that the $9R$ stacking sequence coherently extends over about 40 layers of close-packed planes.

The experiment with the first crystal showed that below 80 K in addition to the long-range-ordered $9R$ structure other polytype sequences are present as short-range-correlated stacking arrangements, i.e., fcc and hcp. The intensity ridge indicates the presence of a great number of stacking faults. Within the framework of polytype ordering[8] this structural feature can be described by a disordered polytype. It should be emphasized that in terms of integrated intensities the diffuse scattering observed corresponds within the same order of magnitude (or even more) to the intensities contained in the sharp $9R$ reflections.

A similar experiment was done with the second crystal. The crystal was cooled down to 70 K. Scans along [101] and [201] showed essentially similar features as in the first crystal. The relative amount, however, of hcp and $9R$-type short-range-order intensity was somewhat increased when compared to the sharper $9R$ reflections.

A further cooling to 30 K of both crystals induced an overall increase of the whole intensity pattern by a factor of 1.5. Within the errors neither a peak narrowing nor a preferential increase of a short-range-order intensity could be observed. Finally, a cooling to 20 K induced no further intensity changes.

The third crystal was first cooled down to 78 K and annealed for a few days. Scans along [101] revealed low and diffuse intensities with broad maxima near hcp, fcc, and $9R$ positions. At this stage only a small part of the bcc lattice (a few percent) had transformed as shown by the intensity of the fundamental bcc reflections. A further cooling to 60 K induced a more drastic increase of the (110) bcc "rocking curve" as observed in the previ-

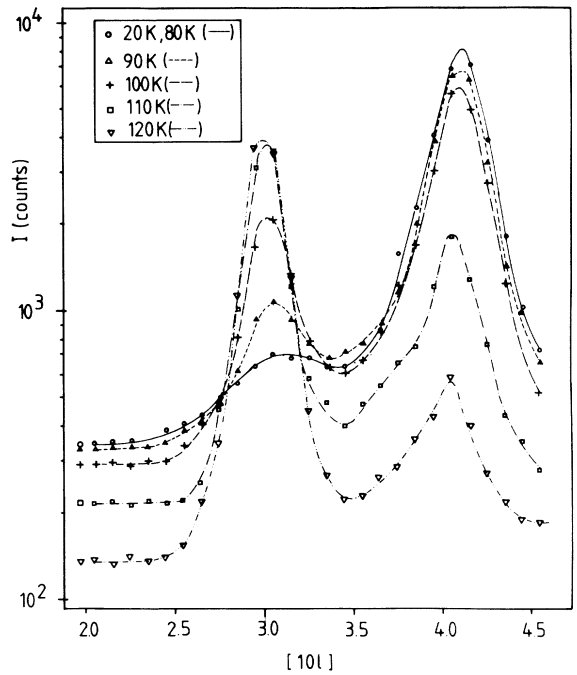

FIG. 3. Intensity distribution in a logarithmic scale near (103) and (104) 9*R* positions during heating from 20 to 120 K in the second crystal. The figure shows the narrowing and increase of the intensity distribution at the (103) point. Furthermore, the decrease and disappearance of the intensity ridge along [101] can be seen on the left-hand side of the figure.

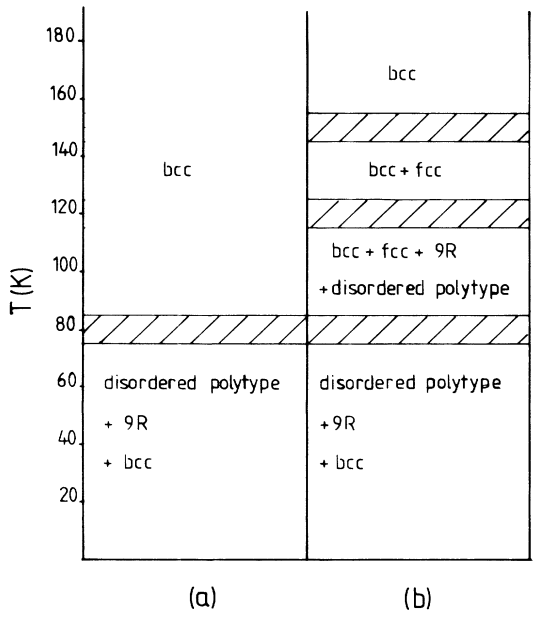

FIG. 4. Schematic representation of the succession of phases observed in lithium as a function of temperature (*T*). The phase boundaries depend on the thermal history of the specimens and are indicated by hatched areas. (a) During cooling and (b) during heating.

ous case; i.e., the mosaic structure of the bcc lattice increased to 5° whereas in the two cases before a broadening to 1.5° was observed. Scans along [101] showed again similar features as with the first two crystals but in addition this time the fcc-type intensities were increased and had a nearly resolution-limited width.

Furthermore, heating all crystals from low temperatures to 80 K induced no noticeable intensity changes. On further heating the fcc intensities grew and narrowed at the expenses of the diffuse scattering and the 9*R* reflections (Fig. 3). At 120 K nearly no 9*R* phase and no diffuse ridge were left and a perfect fcc lattice coexisting with the bcc matrix was observed. It should be emphasized that the reflections of the bcc lattice remained unchanged during the formation of the fcc structure. Upon further heating the fcc peaks diminished near 150 K until about 180 K the original bcc single crystal was recovered (yet with a greater mosaic spread). At about 250 K, however, all single crystals disintegrated into polycrystalline specimens even upon slowly heating. This effect has been observed also by others and should be investigated separately.[3,9]

The present experiment was performed on three crystals where somewhat different cooling procedures were applied. Figure 4 gives a schematic representation of the different phases observed in this experiment. Below 80 K in all cases a considerable amount of diffuse scattering was observed together with a 9*R* structure showing a stacking correlation of longer range. The diffuse scattering is characteristic for the occurrence of a great number of stacking faults (disordered polytype) and of other polytypes as short-range-correlated stacking sequences. The diffuse intensity ridge extends approximately from the (1,0,10) to the (1,0,$\bar{1}$0) point. The ridge intensity is therefore modulated along the (101) direction. Individual stacking faults as found in hcp cobalt, however, would induce an intensity ridge along the whole [101] direction.[10] It follows that in the present case the stacking faults ascribed to the disordered polytype structure are not randomly distributed within the lattice but rather form "clusters." These clusters may consist of arrangements of close-packed planes, where the stacking sequence is disordered and extends on the average over several lattice constants. From the finite range of the intensity distribution on the (101) line an average size for the disordered regions of 3–5 lattice planes may be evaluated. This last finding of disordered stacking sequences corroborates the presence of a disordered polytype phase as an individual structural entity within the family of stacking polytypes.

On heating the complex structural state transforms above 80 K to a perfect fcc lattice coexisting with the bcc matrix. This transition to a fcc lattice has phenomenologically some similarity with a disorder-order transformation as observed in binary alloys, i.e., a sharp intensity component grows out from a short-range-order intensity. Moreover, this "ordering" of the stacking sequences has only a small hysteresis, i.e., the mixed poly-

type phase is formed just below 80 K and "polytype ordering" starts just above. This indicates that in Li the transition between different polytype structures does not involve strong coherency stresses.

The experiment further shows that above 80 K the fcc structure is a stable configuration. Below 80 K, however, the observation of a disordered polytype structure shows the near degeneracy between the hexagonal (H) and cubic (K) stacking sequences. The complex polytype state with different short-range-ordering tendencies may therefore result from a competition between the H and K ordering tendencies within a narrow temperature range.

Furthermore, the simultaneous observation of a long-range-ordered $9R$ structure and of a disordered polytype seems to be in contradiction with a complete degeneracy of the H and K stackings favoring indeed a disordered polytype state. Geometrically the $9R$ structure can be derived from a fcc lattice by the creation of a stacking fault after each ABC sequence. This fault increases the number of H planes in the lattice and its formation is therefore favored by the near degeneracy of H and K. On the other hand, the formation of a coherent fcc nucleus within a bcc structure engenders a macroscopic shear of the bcc matrix (Kurdjonov-Sachs shear)[11] and induces strong coherency stresses. This shear can drastically be reduced by the insertion of a stacking fault on every third plane of the fcc structure (Fig. 5). The $9R$ structure may be therefore formed in cases where the loss of energy due to the insertion of stacking faults into a fcc lattice is compensated by the gain of elastic energy due to lower coherency stresses between $9R$ and the bcc matrix.[12] This conclusion is corroborated by the observation of the more drastic increase of the (110) bcc rocking curve in the third crystal, where a fcc structure is observed as a long-range-correlated stacking sequence already during the cooling procedure, i.e., the fcc structure induces greater coherency stresses than the $9R$ structure when transformed out of the bcc matrix.

On the other hand, the fcc formation above 80 K from a polytype ordering process occurs without the creation of observable coherency stresses. This indicates that this process corresponds indeed to a rearrangement of stacking sequences within the polytype phase without affecting the bcc matrix.

In summary, we have found in Li a disordered polytype structure which coexists with a $9R$ structure below 80 K. Above 120 K a perfect fcc phase is observed. This result indicates that the energy difference between the H and K stackings changes within a narrow temperature range. At lower temperatures the energies connected with the H and K stackings seem to be degenerate.

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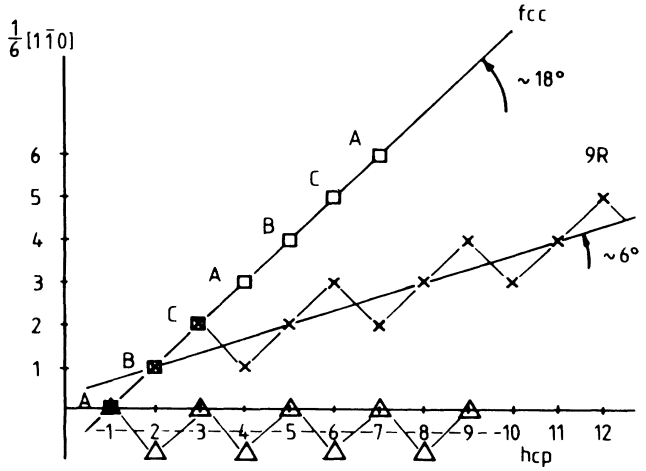

FIG. 5. Schematic representation of the displacements of (110) bcc planes geometrically necessary in order to obtain fcc and $9R$ nuclei, respectively. The formation of both structures induces a macroscopic shear of the bcc matrix. The shear angle for $9R$ ($\sim 6°$) is much smaller than for fcc ($\sim 18°$). The ordinate gives the values for the displacements in units of $\frac{1}{6}[110]$ bcc and the abscissa gives the numbers of consecutive (110) planes with a lattice spacing of $\frac{1}{2}[110]$ (the ordinate and the abscissa are not drawn on the same scale). The displacements necessary for the formation of a hcp structure are also represented. It appears that the hcp formation within a bcc matrix induces no long-wavelength shear.

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