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Influence of plastic deformation on the martensitic phase transformation in lithium

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The influence of plastic deformation on the phase transition behavior of lithium is investigated by neutron scattering techniques. Plastic deformation about 30° above the transformation temperature (74 K) does inhibit the phase transformation even down to low temperatures. On the other hand, below the phase transition temperature plastic deformation favors the phase transformation. The amount of the low-temperature phase is increased but the structure obtained after severe plastic deformation is no longer $9R$. The diffraction data indicate the formation of a polytype where the stacking sequence of close packed planes is disordered. [S0163-1829(97)05101-1]

INTRODUCTION

The alkali metals Na and Li and also the alloy LiMg undergo martensitic phase transformations from a high-temperature bcc phase to close packed structures at low temperatures. This transformation was investigated in a series of neutron scattering experiments in recent years.[1–7]

The experiments revealed complicated low-temperature phase diagrams exhibiting the simultaneous presence of different polytypes of close packed structures in these simple metallic systems. In Na a faulted hcp (AB) phase in connection with the long period $9R$ ($ABCBCACAB$) structure is observed.[4,5] The $9R$ structure is also found in Li (Refs. 1–3) but simultaneously with the $9R$ Bragg reflections strong diffuse scattering is observed. This diffuse scattering was ascribed to the formation of a disordered polytype phase. In Li no hcp phase is found. On heating the $9R$ structure and the disordered polytype partially transform to a fcc (ABC) structure before the bcc phase is recovered at higher temperatures. In LiMg only sharp reflections corresponding to the $9R$ structure could be detected.[7]

The alkali metals are therefore characterized by the formation of different sequences of close packed polytype structures at low temperatures. Energetically the different close packed polytypes are nearly degenerate.[8]

The question arises why simple alkali metals exhibit complex phase diagrams. In all three systems the phase transformation is not complete but all low-temperature polytype structures coexist with the bcc matrix. Therefore, it may be conjectured that coherency stresses between the bcc matrix and the low-temperature phases may influence the phase diagram and the structures observed. Recent theories have indeed related the occurrence of the $7R$ martensite in the martensitic phase transformation in NiAl to the presence of elastic interactions inducing the formation of this adaptive martensite.[9] If coherency stresses are responsible for the great variety of polytype structures in alkali metals then a reduction of these stresses may have an influence on the polytype structures observed, i.e., a transition from one stacking sequence to another may occur.

In recent work we investigated the influence of an *elastic* deformation of the bcc matrix on the phase transformation in Li metal.[10] Experimentally such an influence has never been investigated in alkali metals. In the literature only the influence of hydrostatic pressure has been reported, i.e., hydrostatic pressure increases the transition temperature in Li but lowers it in Na.[11,12]

A uniaxial elastic deformation was applied—i.e., a compression along the [001] direction inducing a lattice expansion along [110] directions. This deformation lowers the coherency stresses between the phases. It was found that such a uniaxial elastic deformation has a significant positive effect on the phase transition behavior. In all cases investigated the uniaxial elastic deformation promotes the phase transition and especially is able to induce the transformation even at temperatures above 82 K. In virgin Li crystals the transition generally occurs below 74 K when the transformation is induced by temperature decrease.[13,17]

On the other hand, in Li metal the structures of the low-temperature phases remained unchanged in all cases of elastic deformation and the $9R$ structure and the disordered polytype phase were still observed. The low-temperature structures found in Li are therefore stable with respect to an elastic deformation.

During the course of this last experiment a Li crystal was also *plastically* deformed. In agreement with the seminal work of Barrett[13] we observed a significant increase of the volume fraction of the low-temperature phase when the Li crystal was subjected to severe plastic deformation at low temperatures. The observed diffraction lines of the low-temperature phase, however, could not be related to hcp and $9R$ structures. The experiment was performed using an aluminum sample container and aluminum diffraction lines restricted the available reciprocal space region. Therefore, no clear decision on the low-temperature structure could be obtained.

In the present work we report on a more systematic investigation of the influence of *plastic* deformation on the phase transition behavior in Li. In the literature general arguments are put forward that martensite will preferentially nucleate near defects and especially near dislocations. It is assumed that the lattice distortion around the dislocation will lower the nucleation energy of the martensite.[14–16] The concept of a localized soft mode—i.e., a soft lattice vibration in the vicinity of a defect—is also discussed as a possible mechanism for martensitic nucleation.[15] From these arguments it follows that an increase of the defect density in a system should have a significant effect on the nucleation behavior during a martensitic transformation. Plastic deformation induces an increase of the dislocation density in a metal and therefore an investigation of the influence of a plastic deformation on the phase transition behavior should yield information whether the martensite preferentially nucleates in the strain field of dislocation cores or not.

Moreover, both in the early work of Barrett[13] and in our recent experiment[10] the results showed an increase of the relative amount of the low-temperature phase when the crystal was plastically deformed at temperatures below the transition temperature. However, Barrett reported to have induced the formation of a fcc structure in Li by plastic deformation whereas in our recent work we could not make a clear structural assignment. In order to resolve the question whether plastic deformation changes the structures of the low-temperature phases in Li we have reinvestigated this point under more favorable experimental conditions. The sample container was made of vanadium which significantly improved the background situation—i.e., induced a flat background—for this experiment.

EXPERIMENT

Plastic deformation was applied to lithium crystals using a similar device as described in Ref. 10. A teflon piston is driven by the pressure of helium gas within a closed-cycle cryostat. The top of the teflon piston is covered by cadmium. The sample is mounted in a cylindrical vanadium container whose axis is in line with the axis of the piston.

Cylindrical single crystals of lithium with a diameter of 5 mm and a height of 15 mm were used as samples. The crystals were mounted with a cubic [001] direction along the axis of the piston and perpendicular to the scattering plane.

The neutron scattering measurements were performed on the triple axis spectrometer VALSE located at a cold neutron guide position of the Laboratoire Léon Brillouin in Saclay. Pyrolytic graphite crystals were used both as monochromator and analyzer. The experiment was performed using an incident neutron wavelength of 2.3 Å . In order to eliminate higher order contaminations a pyrolytic graphite filter was put into the incident beam. The collimations were 30 min throughout.

RESULTS

A. Plastic deformation at 100 K

A virgin bcc Li single crystals was subjected to severe plastic deformation at 100 K by application of a uniaxial pressure of 84 MPa. The single crystal was transformed to a polycrystalline system and Debye-Scherrer lines were observed corresponding exclusively to reflections of the bcc structure. Rocking scans over a wide angular range (about 180°) did not show any strong variation of the (110) bcc reflection. Likewise the sample was tilted out of the original (001) orientation by (+/−)5 °, 10 °, and 15 ° and similar rocking scans were performed showing again no significant variation of the (110) bcc reflection thus indicating the absence of a pronounced texture in the polycrystalline system. No indication of a phase transformation was found at 100 K. Subsequent cooling down to 40 K likewise did not induce any phase transformation and at 40 K only bcc Debye-Scherrer lines could be observed. In particular, even after careful search by radial and rocking scans no intensity was found at reciprocal lattice positions where the strong (009)-9*R* reflection should develop.

The experiment was repeated with a second bcc Li single crystal and again after severe plastic deformation at 100 K no transformation occurred down to low temperatures.

B. Plastic deformation near T_c

A virgin bcc Li single crystal was plastically deformed near 74 K by application of a uniaxial pressure of 43 MPa. The single crystal was destroyed but this time a phase transition occurred as borne out by the appearance of the (009)-9*R* Debye-Scherrer line of the low-temperature phase. Rocking scans along this line showed the absence of a pronounced texture in the polycrystalline material.

Further cooling to 40 K induced a further intensity increase of the (009)-9*R* reflection by about 20%. Subsequent plastic deformation at 40 K induced an increase of the volume fraction of the low-temperature phase by about 15%. The Debye-Scherrer lines of the system were investigated in more detail at 40 K indicating the formation of the 9*R* structure. Figure 1 shows data with peaks corresponding to (101), (104), (105), and (009) 9*R* reflections, respectively. From the intensities of the (009) 9*R* and (110) bcc reflections and from a comparison with the results of Ref. 6 a volume fraction of the low temperature phase of about 70% was evaluated.

C. Plastic deformation below T_c

A virgin Li crystal which had transformed near 70 K was subjected to severe plastic deformation at 60 K by application of a pressure of 84 MPa. The plastic deformation destroyed the single crystal. Rocking scans over a wide angular range were performed at (110) bcc and (009)-9*R* positions but no strong intensity variation was observed indicating again the absence of a pronounced texture in the deformed material.

In order to investigate the low-temperature structure radial scans over the accessible *Q* range were performed. The results are shown in Fig. 2. The diffraction data give evidence of a strong (009)-9*R* reflection indicating a large amount of the low-temperature phase. However, besides the (110) bcc reflection no other reflections could be found within the reciprocal space region investigated. Figure 2 shows only a strong reflection at the (009)-9*R* position together with the (110) bcc reflection of the matrix. Scans were performed over a larger *Q* range as the one depicted in Fig. 2 but no intensity corresponding to a (200) fcc reflection could be detected. The system was then heated up to 150 K

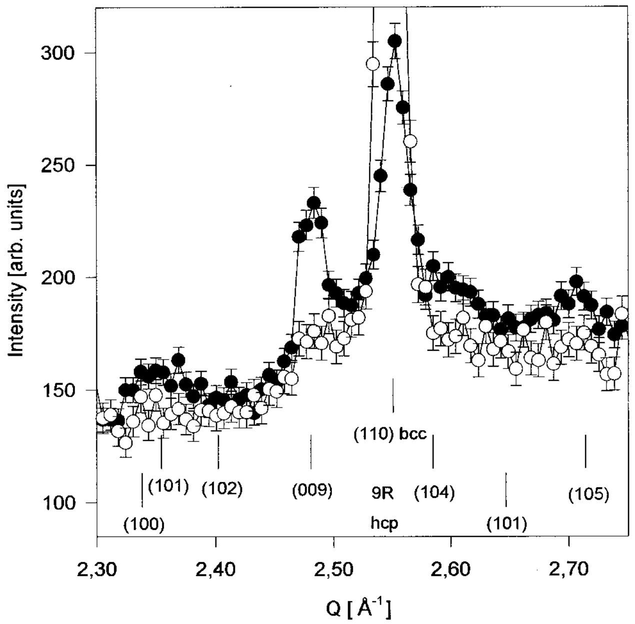

FIG. 1. Radial scan performed at 40 K in a Li crystal, plastically deformed near 74 K then cooled down to 40 K and again subjected to plastic deformation (full symbols) in comparison to the results obtained at 80 K for the same system after a temperature cycle to 200 K where the bcc phase was fully recovered (open symbols). The diffuse background is due to the teflon piston in the pressure cell coming into the beam during the plastic deformation. The vertical bars indicate the expected positions of 9*R*, hcp, and bcc Debye-Scherrer lines. The slight shift of the (104) and (105) 9*R* lines from the ideal positions is qualitatively in accordance with results of Refs. 2 and 6.

and a search for (200) fcc intensities was performed but likewise no fcc reflection could be observed. The backtransformation to the bcc structure started above 110 K.

The experiment was repeated with another Li single crystal but again after severe plastic deformation near 60 K a similar intensity pattern was observed as shown in Fig. 2. From the intensity ratio of the (009) 9*R* and (110) bcc lines a volume fraction of the low temperature phase of about 82% was determined in accordance with the results of Ref. 10.

DISCUSSION

The present experiment has shown that plastic deformation at 100 K does not favor the phase transition even if the plastically deformed system is cooled down to low temperatures. Plastic deformation increases the density of dislocations by a few orders of magnitude and if dislocations act as nucleation centers for martensite formation then some transformation should have been observed. We must, therefore, conclude that static dislocations do not act as nucleation centers for the martensitic transformation in Li. Surprisingly, a high density of dislocations even inhibits the martensitic transformation.

On the other hand, the present experiment yielded the result that plastic deformation near the martensitic start temperature (near 74 K) promotes the phase transition suggesting that in this temperature range plastic deformation facilitates the transformation. It should be mentioned, however, that this has been found to be the case even for an elastic deformation.

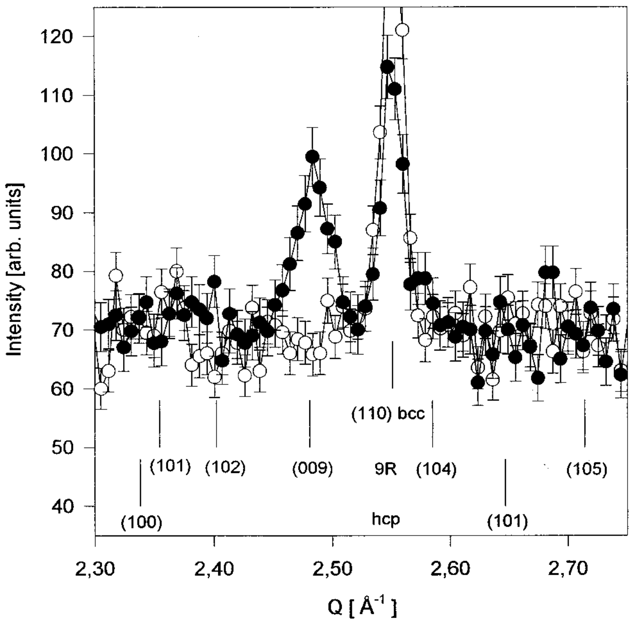

FIG. 2. Radial scan performed at 60 K in a Li system after severe plastic deformation at 60 K (full symbols) in comparison to results at 80 K after a temperature cycle to 200 K where the bcc phase was fully recovered. In this case the teflon piston was better shielded with cadmium and the flat background is due to the vanadium container. The increased width of the (009)-9*R* reflection with respect to the data of Fig. 1 reflects the stronger plastic deformation in the present case. The vertical bars indicate the expected positions of 9*R*, hcp, and bcc reflections. Likewise, no intensity was observed near (200) fcc *Q* positions not shown in the figure.

Any plastic deformation occurs subsequent to an elastic distortion of the system and therefore the promotion of the phase transition observed in the experiment near 74 K may possibly be related to the action of the initial elastic strain which cannot be avoided when the system is plastically deformed. Therefore, it may be conjectured that the 74 K results are induced by the action of the elastic distortion inherently present when plastic deformation is applied. Alternatively, if we admit that static dislocations do not act as nucleation centers as borne out by the results obtained from the 100 K deformation we cannot exclude that dislocations moving during the plastic flow of the system enhance the phase transformation in a temperature range close to the martensitic start temperature.

Moreover, we observed that a plastic deformation well below the martensitic start temperature significantly increases the amount of the low-temperature phase. In this case of severe plastic deformation volume fractions of the transformation product are observed which are significantly higher than those obtained by temperature changes alone and also those induced by elastic deformations. It follows that at low temperatures it is the plastic deformation of the two-phase system which increases the amount of the low-temperature phase.

The question arises why at low temperatures plastic deformation of a system consisting of coexisting phases induces an increase of the amount of the transformation product. If it is accepted that static dislocations do not act as nucleation centers for the phase transition in Li other reasons should be advocated.

First, it is generally accepted that in alkali metals the phase transition is arrested by the presence of coherency stresses. By plastic deformation and plastic flow of both the bcc-matrix and the low-temperature phase the coherency conditions between the two components of the two-phase system change in a way as to lower coherency stresses. The reduction of these stresses which continuously build up during the transition process as long as the system behaves elastically then facilitates further progress of the phase transformation. Secondly, it should be noted that moving dislocations during the plastic deformation may also be responsible for the enhancement of the transformation product.

In systems subjected to severe plastic deformation no $9R$ reflections were observed besides a strong peak at the (009) $9R$ position. Neither hcp nor fcc reflections could be found in these systems despite the fact that a vanadium sample container was used and consequently no contamination from Debye-Scherrer lines of the sample container restricted the available Q range in this experiment. Moreover, a pronounced texture is not present and therefore cannot be responsible for the complete absence of reflections corresponding to other close packed polytype sequences in the data of Fig. 2.

In recent work the low-temperature phase diagram of Li was investigated.[2] It was found that at low temperatures the $9R$ structure appears in connection with a phase where no well defined sequence of close packed planes exists. This disordered polytype phase induces a large amount of diffuse scattering but exhibits no sharp reflections on the $(10l)$ line of the $9R$ reciprocal lattice. A disordered polytype phase is essentially characterized by sharp reflections on the $(00l)$ line of the reciprocal lattice, i.e., a sharp (009) reflection.

The present diffraction results indicate the formation of a disordered polytype structure after severe plastic deformation. This behavior points to an instability of the $9R$ structure in Li with respect to plastic deformation. This result can be related to the near degeneracy of the different stacking sequences of close packed planes in lithium metal as already borne out by its low-temperature phase diagram. The observed disordered polytype structure is induced by plastic deformation but does not necessarily represent a new low temperature phase in a strict thermodynamic sense.

In summary, we found that a high density of static dislocations does not favor the phase transition at all and even suppresses the formation of the low-temperature structure. On the other hand, moving dislocations during the plastic deformation may favor the transformation at lower temperatures. Despite a careful search we found no indication of an fcc structure in Li after plastic deformation at low temperatures. The diffraction data obtained in this experiment indicate the occurrence of a disordered stacking polytype in the deformed material.

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